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TRANSACTIONS.

LIII.—*Contributions to the Chemistry of Caramel. Part I. Caramelan.*

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THE action of heat on sugars produces a mixture of compounds which is usually known as caramel. Caramel products have been used for a long time on account of their colouring properties, and their manufacture has attained a certain degree of exactness, since it is possible to make, at will, colours of varying qualities and different degrees of solubility and stability. The knowledge so gained is largely empirical, and very little is known of the chemical nature of the caramel compounds and of their relations to the parent substance and to one another. The absence of investigation is accounted for partly by the indefinite position of these sub-stances among the carbohydrates and partly by the technical diffi-culties involved. The caramel compounds are very complex, very difficult to separate from one another, and are without definite melting points or other criteria of purity. They are amorphous, yield no crystalline derivatives, and readily form colloidal solu-tions. Our present knowledge of caramel from sucrose is confined, for the most part, to the researches of Gélis (*Ann. Chim. Phys.*, 1858, [iii], **52**, 352; 1862, [iii], **65**, 496), who showed that when sucrose is heated to 180—190° there are formed three products, which he named caramelan, caramelen, and caramelin, the order of their formation following the order of the vowels. Analysis showed that these three products are carbohydrates formed appa-rently by successive dehydration and polymerisation, until in caramelin a substance of high molecular weight and colloidal char-acter is reached. Their formation may be represented, for pur-poses of comparison, by the following equations:

$$\text{(i)} \quad 6C_{12}H_{22}O_{11} - 12H_2O = 6C_{12}H_{18}O_9 \text{ (caramelan)}.$$
$$\text{(ii)} \quad 6C_{12}H_{22}O_{11} - 18H_2O = 2C_{36}H_{48}O_{24} \text{ (caramelen)}.$$
$$\text{(iii)} \quad 6C_{12}H_{22}O_{11} - 27H_2O = 3C_{24}F$$
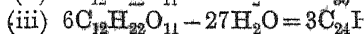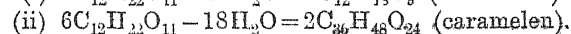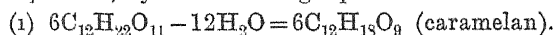
Practically nothing has since been a caramel. For a long time past we hav of the process of the formation of cara -apart from its specific interest, may have of the constitution of cellulose and its relationship to the carbo-hydrates, and especially on the connected problem of the formation of humus, peat, and coal in the soil. Cellulose is generally repre-sented by the formula given by Green (T., 1906, **89**, 811), namely, as a complex based on a $C_6H_{10}O_5$ unit derived from dextrose, the

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units being joined through oxygen atoms (formula I). This view has received support from the observation of Willstätter (*Ber.*, 1913, **46**, 2401) that cellulose passes quantitatively into dextrose when treated with cold concentrated hydrochloric acid, although previous work on the production of ω-hydroxymethylfurfuraldehyde (Fenton, T., 1901, **79**, 361) from cellulose pointed rather to a ketonic structure.
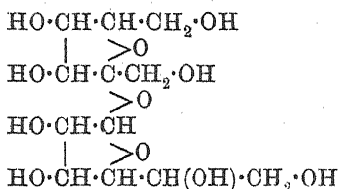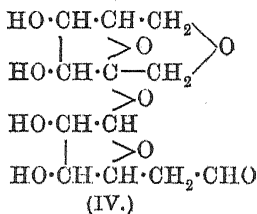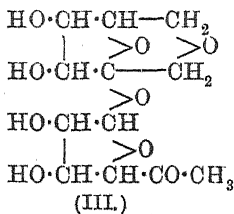
The little evidence available points to sucrose as the precursor of cellulose in the development of plants. The constitution of sucrose is generally represented by Fischer's formula * (II) (*Ber.*, 1893, **26**, 2405). Two possible formulæ for caramelan, based on it, are given (III) and (IV), which explain to some extent our results. The analogy to cellulose (I) is seen and the capacity shown by the caramelan unit to form more complex molecules can readily be explained by the opening up of the butylene oxide linking, union taking place between the oxygen atoms.

$$\begin{array}{l} \text{O---} \\ | \\ \text{HO·CH·CH·CH·OH} \\ \quad | \quad >\!\text{O} \\ \text{HO·CH·CH·CH}_2 \\ \qquad\quad | \end{array}$$
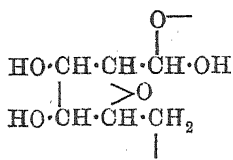
(I.) Cellulose unit group (Green).

$$\begin{array}{l} \text{HO·CH·CH·CH}_2\text{·OH} \\ \quad | \quad >\!\text{O} \\ \text{HO·CH·C·CH}_2\text{·OH} \\ \qquad >\!\text{O} \\ \text{HO·CH·CH} \\ \quad | \quad >\!\text{O} \\ \text{HO·CH·CH·CH(OH)·CH}_2\text{·OH} \end{array}$$

(II.) Fischer's formula for sucrose.

$$\begin{array}{l} \text{HO·CH·CH---CH}_2 \\ \quad | \quad >\!\text{O} \ >\!\text{O} \\ \text{HO·CH·C-----CH}_2 \\ \qquad >\!\text{O} \\ \text{HO·CH·CH} \\ \quad | \quad >\!\text{O} \\ \text{HO·CH·CH·CO·CH}_3 \end{array}$$

(III.)

$$\begin{array}{l} \text{HO·CH·CH·CH}_2\!\!\diagdown \\ \quad | \quad >\!\text{O} \quad\ >\!\!\text{O} \\ \text{HO·CH·C---CH}_2\!\!\diagup \\ \qquad >\!\text{O} \\ \text{HO·CH·CH} \\ \quad | \quad >\!\text{O} \\ \text{HO·CH·CH·CH}_2\text{·CHO} \end{array}$$

(IV.)

Possible formulæ for caramelan, $C_{12}H_{18}O_9$.

By chemical and bacterial action in the soil, cellulose is transformed into humus. This product is generally stated to consist of (*a*) humic acid, $C_{12}H_{20}O_6$, soluble in alkali hydroxides and reprecipitated on addition of acids, (*b*) humin, insoluble in alkaline solutions, requiring fusion with alkalis before solution can be obtained. Very similar humus products are obtained by the hydrolysis of carbohydrates by acids and alkalis. Sestini (*Gazzetta*, 1880, **10**, 121, 240, 355) obtained from sucrose (*a*) soluble sac-

* As there is no evidence to show that the hexose groupings in sucrose retain their original configuration in caramelan, Haworth and Law's recent formula for sucrose (T., 1916, **109**, 1319) has not, for the moment, been employed.

chulmic acid, $C_{44}H_{40}O_{16}$, and (b) insoluble sacchulmin, $C_{44}H_{58}O_{15}$. Bottomley (*Biochem. J.*, 1915, **9**, 260) has recently stated that humic acid and humin are formed from sucrose by heating it to 220°, and suggests that in peat bogs the carbohydrates of decaying organic matter may pass through changes similar to those observed when sucrose is heated to a high temperature, thus, sucrose, caramelan, humic acid, humin, and finally carbonisation (peat, coal). Bottomley also found that artificial humic acid obtained by boiling dextrose with hydrochloric acid had a composition very similar to the natural humic acid prepared from peat.

Résumé of Previous Work on Caramel Compounds.

Gélis (*loc. cit.*) showed that sucrose melted at 160° and if kept at that temperature changed without loss of weight into dextrose and lævulosan, $C_6H_{10}O_5$.

By raising the temperature to 180—190° he obtained the three carbohydrates, caramelan, caramelen, and caramelin. The proportion in which each of these was formed varied with the time of heating and the consequent loss of weight. A loss of 12 per cent. gave mostly caramelan, a loss of 15 per cent. chiefly caramelen, and with a loss of 22 per cent. the product consisted almost entirely of caramelin. These three compounds were separated by extracting the caramelan with 84 per cent. alcohol, in which caramelen and caramelin were insoluble. The caramelen was then removed by extraction with cold water, leaving caramelin, which was soluble only in 60 per cent. alcohol or hot water.

Caramelan, prepared in this way, is described as a brown, brittle solid of a bitter taste. It softens at 108°, is very deliquescent, and very readily soluble in water. The aqueous solution is not precipitated by metallic salts, but silver nitrate and Fehling's solutions are reduced. When treated with an alcoholic solution of lead acetate a compound, $C_{12}H_{16}O_8,PbO$, is precipitated, whilst ammoniacal lead acetate gives $C_{12}H_{16}O_8,2PbO$. Similar preparations were obtained with barium. From analysis of the lead and barium compounds and of caramelan itself, Gélis assigned to it the formula $C_{12}H_{18}O_9$.

Caramelen is described as a brown substance much darker in colour than caramelan and not deliquescent. It reduces Fehling's solution and forms compounds with lead and barium similar to those of caramelan. The composition was found to be $C_{36}H_{48}O_{24}$.

The hot aqueous solution yielded caramelin, which is a colloidal substance described by Gélis as existing in three modifications, A, B, and C, of which A is soluble in cold water, B only in boiling water, and C insoluble in all ordinary solvents. Caramelin A

passes into the modification B on evaporating its aqueous solution, and can thus be separated from caramelen. All three modifications give the same compound with barium, and have therefore the same composition, namely, $C_{96}H_{102}O_{51}$. Caramelin reduces Fehling's solution and is precipitated from solution by almost all metallic salts. It is infusible, very difficult to burn, and much darker in colour than caramelen or caramelan.

Graham (*Journ. Chem. Soc.*, 1862, **15**, 258) prepared pure caramelin by dialysing an aqueous solution of caramel, when unchanged sucrose, caramelan, and caramelen passed through the dialyser and caramelin remained behind.

Caramelin prepared in this way had a similar composition, namely, $C_{24}H_{26}O_{13}$, and properties to the caramelin prepared by Gélis. It is precipitated from solution by metallic salts, and if its aqueous solution is evaporated in a vacuum it remains soluble, but if evaporation takes place at 100° an insoluble product is formed which will dissolve only in alkali hydroxides.

The molecular weight of 'caramel' probably consisting largely of caramelin, was determined by Gladstone and Tribe, who found the value 1700, corresponding with Gélis's formula.

In 1899 caramelan was examined by Stolle (*Zeitsch. Rübenzucker Industrie*, 1899, **49**, 800; 1901, **51**, 836; 1903, **53**, 1149), who prepared it by heating sucrose at 180—190° until there was a loss of weight of 12 per cent. He found that no carbon dioxide or other products were formed until the temperature rose above 180°. Caramelan is therefore formed by simple loss of water, and by analysis and a molecular weight determination Stolle confirmed the molecular formula, $C_{12}H_{18}O_9$. On hydrolysis, a hexose similar to dextrose was obtained which could not be identified.

In 1906 Trillat (*Zeitsch. Rübenzucker Industrie*, 1906, **56**, 95) examined the volatile products formed when sucrose is heated. At 200°, 0·1—0·3 per cent. of formaldehyde was obtained. At 100°, traces only were apparent even after twenty-four hours, but at 150° it was perceptible even in a few minutes. Trillat concluded that caramel is really a combination of the polymerised products of formaldehyde.

The work described in the present communication deals chiefly with the caramelan from sucrose. Although a study of the action of heat on dextrose would seem to be a simpler problem, the products obtained, whilst apparently no less complex, proved very much more difficult to separate than those from sucrose. The methods previously given for the preparation of caramelan have been examined. The composition $C_{12}H_{18}O_9$ has been confirmed,

but many of the results obtained point to $C_{24}H_{36}O_{18}$ as the molecular unit. The presence of four hydroxyl groups in the C_{12} formula has been established by the preparation of esters, of which the explosive nitrate is of interest. Compounds with phenylhydrazine and semicarbazide have been prepared, but although these point to the presence of a carbonyl grouping, their composition does not correspond with that of a simple derivative of $C_{12}H_{18}O_9$. Analysis shows that dehydration and condensation have simultaneously taken place, a characteristic phenomenon observed also in all the cases of oxidation which have been studied. On hydrolysis with dilute acids, dextrose and methylfurfuraldehyde have been obtained and a humus product. The action of concentrated acid does not give simple sugars, as with cellulose, but results in further dehydration to caramelin.

Experimental.

The Preparation of Caramelan.

Preliminary experiments were undertaken to test the accuracy of the statement that sucrose, if heated at 170—180° until there is a loss of weight of 12 per cent., loses water only. This statement implies that sucrose passes quantitatively into caramelan according to the equation:

$$C_{12}H_{22}O_{11} = C_{12}H_{18}O_9 + 2H_2O,$$
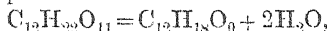
which requires a loss of weight of 10·5 per cent. (the figure 11·77 given by Stolle being calculated on the weight of caramelan instead of on that of sucrose). The experiment described below shows that with a loss in weight of 10 per cent. and even at 168° other products, besides water, are formed. A weighed quantity of sucrose was heated in a boiling tube attached to a wash-bottle containing 12 per cent. hydrochloric acid to dissolve any furfuraldehyde formed. At 168° (thermometer placed in the sugar) oily drops began to distil over which dissolved in the acid. The heating was continued at this temperature for two and a-half hours. On testing the hydrochloric acid solution with phloroglucinol, a black precipitate was obtained showing the presence of furfuraldehyde. Pungent acid vapours and carbon dioxide were also evolved. The loss of weight was 10 per cent., and this cannot all be due to loss of water. It was found, however, that if sucrose is heated at 170—180° until the loss of weight is 12 per cent., practically pure caramelan free from sucrose and higher caramel products was obtained. This was the method of preparation finally adopted, 300 grams of sucrose requiring about four hours' heating.

Considerable quantities of caramelan were also prepared according to Gélis's method, which is more tedious to carry out than the

one described above, although the time of heating is greatly reduced owing to the higher temperature employed. The details are as follows:

Three hundred grams of sucrose were heated in a porcelain beaker at 180—190° and stirred continually with the thermometer. After two hours, the loss of weight was 12 per cent. The contents of the beaker were dissolved in water, the solution filtered, and the filtrate evaporated to a syrup, which was dried at 100° and finely powdered. The powder was treated with boiling 84 per cent. alcohol and filtered hot, the filtrate being evaporated on the water-bath and finally dried at 120°.

Caramelan, prepared in these ways, is a brown, gritty powder, very hygroscopic, but not viscid unless damp. When quite dry, its melting point is 136°, but if at all moist it begins to soften at 100°. It is very readily soluble in water, fairly so in 84 per cent. alcohol, pyridine, methyl alcohol, or hot glacial acetic acid; insoluble in ether, alcohol, or benzene. It reduces silver nitrate and Fehling's solution. A concentrated aqueous solution acidified with hydrochloric acid gives a red precipitate on the addition of resorcinol, which is soluble in alcohol or alkalis. Phloroglucinol gives a similar precipitate, but of a deeper colour.

In order to prepare a pure sample of caramelan for analysis, attempts were made to precipitate it from aqueous solution by means of alcohol. The substance, however, separated as a syrup which could not be collected, but it was found that if the solution contained acetic acid or ammonia, a flocculent precipitate was obtained which settled well and could be collected and washed with alcohol. After drying, it formed a buff-coloured powder much paler in colour than crude caramelan:

0·0993 gave 0·1707 CO_2 and 0·0567 H_2O. C = 46·9; H = 6·3.

$C_{12}H_{18}O_9$ requires C = 47·1; H = 5·9 per cent.

Stolle found C = 46·2; H = 6·4 per cent.

Molecular-weight determinations of caramelan and some of its derivatives were also carried out. These will be discussed later.

The Esters of Caramelan.

The formula $C_{12}H_{18}O_9$ indicates that the eight hydroxyl groups in sucrose have been reduced to four in caramelan. This was verified by the preparation of the following esters:

Caramelan Tetra-acetate, $C_{12}H_{14}O_9(CH_3 \cdot CO)_4$.—A mixture of 20 grams of caramelan, 40 grams of fused sodium acetate, and 60 grams of acetic anhydride was boiled for two hours under a reflux condenser. The contents of the flask became very dark-coloured. On pouring into water a voluminous, brown precipitate

formed, which was washed several times by decantation. It was dissolved in hot alcohol and precipitated by the addition of salt solution. After washing and drying in a vacuum, the acetate formed a yellow powder insoluble in water or ether, but soluble in benzene, hot alcohol, or glacial acetic acid. On heating, it shrinks at 96° and melts at 107°. It reduces silver nitrate and Fehling's solution. (Found, $C = 51·0$; $H = 5·8$. $C_{20}H_{26}O_{13}$ requires $C = 50·6$; $H = 5·5$ per cent.)

Stolle (*loc. cit.*) obtained this compound in 1899, and his description agrees, with slight exception, with that of the above preparation.

Caramelan Tetrabenzoate, $C_{12}H_{14}O_9(C_6H_5 \cdot CO)_4$.—Five grams of caramelan dissolved in 30 c.c. of dry pyridine were mixed with 10 grams of benzoyl chloride diluted with the same solvent. After remaining for twelve hours, the mixture was poured into water, when a tarry precipitate formed which was dissolved in acetone and precipitated by salt solution. The precipitate was washed with water and dried in a vacuum. The benzoate formed a pale buff-coloured powder melting at 105—108°, soluble in acetone, chloroform, alcohol, or benzene, and insoluble in water, ether, or light petroleum :

0·1497 gave 0·3630 CO_2 and 0·0661 H_2O. $C = 66·1$; $H = 4·9$.

$C_{40}H_{34}O_{13}$ requires $C = 66·5$; $H = 4·7$ per cent.

Caramelan Tetranitrate, $C_{12}H_{14}O_9(NO_2)_4$.—Five grams of caramelan, cooled in ice, were treated with 50 c.c. of fuming nitric acid, in which it dissolved quite readily, and 25 c.c. of concentrated sulphuric acid were gradually added. A solid clot formed, which was washed with ice-water by decantation after the bulk of the acid had been poured off. When dried, the product was dissolved in hot alcohol, from which it separated on cooling. The nitrate forms a yellow powder which inflames violently on warming, resembling nitrocellulose in this respect. It is very readily soluble in ether, alcohol, or benzene, but insoluble in water. The nitrate decomposes so easily on warming that it was impossible to analyse it by the ordinary method. The nitrogen content was therefore estimated by the nitrometer :

0·1163 gave 21·4 c.c. NO at 14° and 758 mm. $N = 11·0$.

$C_{12}H_{14}O_{17}N_4$ requires $N = 11·5$ per cent.

The Molecular Weights of Caramelan and its Esters.

Stolle, as the result of a single determination in aqueous solution, obtained a value for the molecular weight of caramelan corresponding with the formula $C_{12}H_{18}O_9$. The following experiments do not confirm this.

(*a*) Caramelan. Solvent, water. $C_{12}H_{18}O_9$ requires M.W. $= 306$.

Concentration of solution, per cent.	Weight of substance taken.	Depression of the freezing point.	Molecular weight.
0·8	0·2477	0·039°	385
2·9	0·8657	0·103°	509
3·3	0·8959	0·113°	539
4·1	1·2345	0·138°	546

(*b*) Caramelan tetra-acetate. $C_{20}H_{26}O_{13}$ requires M.W. $= 474$.

(i) 0·475 in 31 benzene gave $\Delta t = +0·041°$. M.W. $= 972$.

(ii) 0·8365 in 31 benzene gave $\Delta t = +0·072°$. M.W. $= 972$.

(*c*) Caramelan tetrabenzoate, $C_{40}H_{24}O_{13}$, requires M.W. $= 722$.

(i) 0·3135 in 41·8 ethylene dibromide gave $\Delta t = -0·042°$. M.W. $= 2107$.

(ii) 0·7439 in 41·8 ethylene dibromide gave $\Delta t = -0·087°$. M.W. $= 2414$.

The results indicate, in the case of caramelan and its acetate, a molecular weight of twice that corresponding with the formula $C_{12}H_{18}O_9$. They may be explained by the well known association phenomena shown by polyhydroxy-compounds in the limited range of solvents available, and the fact that the benzoate gives a value three times that of the simple formula may be held to support this view. Several observations described below, however, are best explained on the assumption of the double formula, and, although it is not possible to decide definitely, a review of the evidence as a whole points to the formula $C_{24}H_{36}O_{18}$ as the correct one.

The Aldehydic or Ketonic Character of Caramelan.

Caramelan, besides reducing silver nitrate and Fehling's solution, gives red precipitates with resorcinol and phloroglucinol. The reaction with these phenols is generally described as characteristic of ketoses, and points to the presence of a ketonic group in caramelan which should give the usual derivatives. Caramelan, when warmed with phenylhydrazine, gives an insoluble compound which readily forms colloidal solutions, but although a number of preparations were made, under varying conditions, none of them had the composition of a simple hydrazone.

Analysis of all the derivatives showed that polymerisation to a C_{24} molecule had taken place, together with a varying loss of water. An obvious way to avoid this dehydration would be to work with one of the esters, but although the acetate, when treated with phenylhydrazine, yields an insoluble compound, this has not yet been obtained sufficiently pure for analysis owing to the difficulty

of separating the hydrazone from unchanged acetate, since both are soluble in the same solvents.

(I) *Reaction with Phenylhydrazine in the Presence of Acetic Acid.*—Five grams of caramelan were dissolved in water and 4 grams of phenylhydrazine in acetic acid solution added, together with 2 grams of sodium acetate. The mixture was warmed on the water-bath and after twenty minutes a precipitate began to form. The precipitate settled well after the addition of brine and was washed with water containing acetic acid. After being dried, it formed a dark red, infusible powder, sparingly soluble in alcohol or pyridine. A second preparation was made, using only half the quantity of phenylhydrazine. Analysis of these two derivatives gave the following results:

(i) 0·0996 gave 0·1972 CO_2 and 0·0494 H_2O. C=54·2; H=5·5.
 0·1407 ,, 4·1 c.c. N_2 (moist) at 13° and 770 mm. N=3·5.

(ii) 0·1035 ,, 0·2071 CO_2 and 0·0544 H_2O. C=54·6; H=5·8.
 0·2440 ,, 7·4 c.c. N_2 (moist) at 23° and 770 mm. N=3·8.
 $C_{30}H_{38}O_{15}N_2$ requires C=54·1; H=5·7; N=4·2 per cent.

A compound, $C_{30}H_{38}O_{15}N_2$, would be formed from caramelan according to the equation:

$$2C_{12}H_{18}O_9 + C_6H_5 \cdot NH \cdot NH_2 = C_{30}H_{38}O_{15}N_2 + 3H_2O.$$

II. *Reaction with Phenylhydrazine in the Presence of Sulphuric Acid.*—The reaction with phenylhydrazine was next carried out in the presence of sulphuric acid to confirm, if possible, our first impression that the low value found for nitrogen indicated, not the formation of a hydrazone, but a condensation similar to the carbazole reaction, ammonia being eliminated (Dorée, T., 1909, **95**, 653). The compound obtained was similar to that described above, but on analysis:

0·1159 gave 0·2666 CO_2 and 0·0501 H_2O. C=62·7; H=4·8.
0·4070 ,, 18·6 c.c. N_2 (moist) at 15° and 758 mm. N=5·3.
 $C_{30}H_{28}O_{10}N_2$ requires C=62·4; H=4·8; N=4·9 per cent.

After solution in pyridine and fractional precipitation by alcohol the nitrogen content remained unaltered:

0·2055 gave 9·4 c.c. N_2 (moist) at 18° and 770 mm. N=5·3.

The substance would thus appear to be a definite compound. It may be formed from caramelan according to the equation:

$$2C_{12}H_{18}O_9 + C_6H_5 \cdot NH \cdot NH_2 = C_{30}H_{28}O_{10}N_2 + 8H_2O.$$
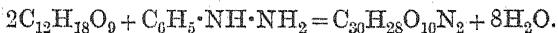
This indicates that two molecules of caramelan, under the stronger condensing action of the sulphuric acid, have lost seven molecules of water while reacting with phenylhydrazine. A similar

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proportionate loss is found in the condensation of caramelan to humic acid, $C_{24}H_{22}O_{11}$ (see below):

$$2C_{12}H_{18}O_9 = C_{24}H_{22}O_{11} + 7H_2O.$$
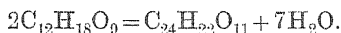
(III) *Reaction with Semicarbazide.*—Ten grams of caramelan and 10 grams of sodium acetate were each dissolved in 10—15 c.c. of water, the solutions mixed together, and 6 grams of semicarbazide hydrochloride in 5 c.c. of water added. After warming at 60° for half an hour, the mixture was allowed to remain for twenty-four hours. On pouring into salt solution a brown precipitate appeared, which was dried, washed free from salt with diluted alcohol, and purified by solution in pyridine and reprecipitation by alcohol:

0·1034 gave 0·1986 CO_2 and 0·0507 H_2O.   C = 52·4 ; H = 5·4.

0·2357   „   11·0 c.c. N_2 (moist) at 12° and 752 mm.   N = 5·5.

$C_{37}H_{43}O_{20}N_3$ requires C = 52·4 ; H = 5·1 ; N = 5·5 per cent.

No explanation of the result can be offered, except that a compound of this composition might be formed thus:

$$3C_{12}H_{18}O_9 + NH_2 \cdot NH \cdot CO \cdot NH_2 = C_{37}H_{43}O_{20}N_3 + 8H_2O.$$
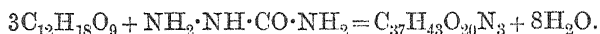
The Action of Acids on Caramelan (3 *per cent. Sulphuric Acid,* 12 *per cent. Hydrochloric Acid, and* 40 *per cent. Hydrochloric Acid*).

Caramelan being thus recognised as an anhydro-derivative of sucrose, it was important to ascertain whether, under the action of acids, it became hydrolysed to simpler carbohydrates. The results show that with dilute sulphuric acid, caramelan does yield some dextrose, together with methylfurfuraldehyde and a humic acid.

(i) *Three per Cent. Sulphuric Acid.*—One hundred grams of caramelan were warmed on the water-bath for eighteen hours with 1 litre of 3 per cent. sulphuric acid. The solution, which was dark and opaque, showed little change in colour as the heating continued. A dark brown substance separated, which after washing with water and drying weighed 14 grams (product *A*). It resembled the humic acid obtained by Conrad and Gutzeit (*Ber.*, 1885, **18**, 443) and others from carbohydrates. The filtrate from this was examined as described below (filtrate *B*).

The *insoluble product A* was a brown powder insoluble in all solvents. It had no reducing properties. When treated with dilute alkali hydroxides it formed a red solution, which after neutralisation gave insoluble lead and barium salts:

(i) 0·1116 gave 0·2417 CO_2 and 0·0510 H_2O.   C = 59·1 ; H = 5·0.

(ii) 0·1290   „   0·2784 CO_2 „   0·0557 H_2O.   C = 58·9 ; H = 4·8.

$C_{24}H_{22}O_{11}$ requires C = 59·3 ; H = 4·5 per cent.

This compound could be formed from caramelan according to the equation:

$$2C_{12}H_{18}O_9 = C_{24}H_{22}O_{11} + 7H_2O.$$
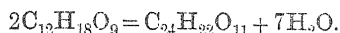
By boiling dextrose with 7 to 12 per cent. hydrochloric acid, Bottomley (*Biochem. J.*, 1915, **9**, 260) obtained an artificial humic acid of the composition $C = 60\cdot74$; $H = 5\cdot13$ per cent. He also found that the natural humic acid obtained from peat after purification with alcohol gave $C = 60\cdot37$; $H = 5\cdot39$. The product prepared from caramelan is, therefore, very similar in composition to both the artificial and natural humic acid. In order to characterise this substance still further, advantage was taken of an observation subsequently made (p. 604) that 7 per cent. nitric acid has both an oxidising and nitrating action on many of these complex carbohydrates, and that, in the case of caramelan it yields a compound, $C_{23}H_{23}O_{14}N$. The composition of this substance suggested that it might be a derivative of a previously formed humic acid, $C_{24}H_{22}O_{11}$, which, therefore, if similarly treated, should yield the same compound. This hypothesis was confirmed by the following experiment. Five grams of the humic acid were warmed on the water-bath for thirty minutes with 7 per cent. nitric acid, when the colour changed from dark brown to bright red. Carbon dioxide and nitrous fumes were evolved, and if the heating was continued too long the red compound began to pass into solution. When dried, it formed an infusible, red powder, soluble only in alkali hydroxides to a red solution. Insoluble lead and barium salts could be prepared from this solution. The substance reduced silver nitrate and Fehling's solution, and when warmed with zinc dust and potassium hydroxide evolved ammonia. These reactions indicate that the compound is a nitrated derivative of the humic acid, $C_{24}H_{22}O_{11}$:

$0\cdot1332$ gave $0\cdot2522$ CO_2 and $0\cdot0488$ H_2O. $C = 51\cdot6$; $H = 4\cdot1$.

$0\cdot5739$,, $13\cdot6$ c.c. N_2 (moist) at $13°$ and 760 mm. $N = 2\cdot8$.

$C_{23}H_{23}O_{14}N$ requires $C = 51\cdot4$; $H = 4\cdot3$; $N = 2\cdot6$ per cent.

This nitrated compound may be regarded as derived from the humic acid, $C_{24}H_{22}O_{11}$:

$$C_{24}H_{22}O_{11} + HNO_3 + O_2 = C_{23}H_{23}O_{14}N + CO_2.$$
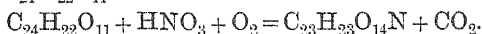
The initial action of dilute nitric acid therefore closely resembles that of hydrochloric and sulphuric acids in that it produces humic acid.

Examination of the Soluble Products of Hydrolysis.—The *filtrate B* from the insoluble humic acid was neutralised with lead carbonate, the lead precipitated with hydrogen sulphide, and the filtrate several times extracted with ether. The aqueous residue from the ethereal extract was concentrated by distillation under

diminished pressure and left a syrup which, after treatment with animal charcoal, became very nearly colourless. This syrup had previously been obtained and examined by Stolle (*Zeitsch. Rüben-zucker Industrie*, 1903, **53**, 1149), who, after working up 600 grams of caramelan, isolated a small quantity of a crystalline sugar from it. In its optical rotation and melting point (93°) it resembled dextrose, but its osazone, although having the composition of a hexose osazone, melted at 197° instead of 206—207° as required for glucosazone (Fischer). By oxidation with dilute nitric acid, *d*-tartaric acid was obtained. With these differences, Stolle considers it doubtful whether the sugar formed from caramelan is really dextrose. In the present case the sugar did not crystallise in a reasonable time. Its solution gave all the qualitative tests described for dextrose identically with those given by a specimen of pure dextrose. It readily gave an osazone after warming for half an hour with phenylhydrazine acetate. This was carefully purified by crystallisation from dilute pyridine, and melted at 206—207° very sharply. Its microcrystalline appearance was identical with that of glucosazone, and it formed mixed crystals without any alteration of form. When mixed with a specimen of glucosazone melting at 206°, the melting point remained unchanged. The syrup, on oxidation with nitric acid (D 1·15), gave saccharic acid, which was isolated as the potassium hydrogen salt. (Found, K = 15·2. $KHC_6H_8O_8$ requires K = 15·7 per cent.)

These observations taken together make it almost certain that the sugar formed by the hydrolysis of caramelan is dextrose.

The *ethereal extract* was acid. On extraction with dilute alkali a dark red solution was obtained which gave a hydrazone and a silver salt, but neither of these could be identified as a derivative of lævulic acid. Stolle recognised the presence of this acid, however, by means of the calcium salt. The ether remaining left a yellow oil which showed all the reactions of methylfurfuraldehyde described in a previous paper (Cunningham and Dorée, *Biochem. J.*, 1914, **8**, 438). It gave a red, and not a black, precipitate with phloroglucinol, soluble in alcohol, and a yellow colour with aniline in alcohol, in these respects differing from furfuraldehyde. It also formed a yellow precipitate with barbituric acid (distinction from ω-hydroxymethylfurfuraldehyde). The presence of methylfurfuraldehyde is thus indicated.

(ii) *Twelve per Cent. Hydrochloric Acid.*—Caramelan was treated with acid of this strength and the distillation carried out according to the Kröber method for the estimation of furfuraldehyde (*J. Landw.*, 1901, **49**, 7). The distillates gave black precipitates with phloroglucinol, insoluble in alcohol, indicating that furfuraldehyde alone was present (Ellett and Tollens, *J. Landw.*, 1905, **53**, 3).

(a) 5·44 Caramelan gave 0·0615 furfuraldehyde phloroglucide Furfuraldehyde = 0·40 per cent.

(b) 4·18 Caramelan gave 0·0390 furfuraldehyde–phloroglucide. Furfuraldehyde = 0·45 per cent.

Previous experiments had shown that such carbohydrates as dextrose, lævulose, starch, and cellulose give constantly about 0·2 per cent. of furfuraldehyde and 1—1·5 per cent. of ω-hydroxy-methylfurfuraldehyde. The above observations show that the latter substance is not formed by caramelan under the conditions employed, and this difference again suggests modifications of the parent sugar during the formation of caramel.

A very considerable *black residue* remained in the flask after these distillations, and as similar products have been obtained previously from sugars, cellulose, and lignocellulose, it was, for comparison, characterised by the method used in these cases (Cross, *Chem. News*, 1881, **44**, 185). The residue was washed until free from acid, and when dry formed a brown powder. This was moistened with water and treated with potassium chlorate and hydrochloric acid, when it immediately turned yellow. The yellow compound was collected, washed, and dried. It dissolved entirely in alkali hydroxides, and was reprecipitated on the addition of acid. Analysis showed that it contained chlorine:

0·0993 gave 0·1475 CO_2 and 0·0334 H_2O. C = 40·5; H = 3·7.

0·1005 ,, 0·0602 AgCl. Cl = 14·83.

$C_{24}H_{29}O_{18}Cl_3$ requires C = 40·5; H = 4·0; Cl = 14·98 per cent.

The compound is therefore probably a chlorinated derivative of a humic acid, and its composition is of the same order as those of the chlorinated humus substances previously obtained. Thus Cross (this Journ., 1880, **38**, 668; T., 1882, **41**, 94) prepared from jute a compound, $C_{20}H_{16}O_{10}Cl_4$, and from esparto pulp a product, $C_{24}H_{16}O_{20}Cl_8$, whilst from cellulose a compound, $C_{22}H_{16}O_{12}Cl_{10}$, was obtained (Gostling, T., 1903, **83**, 190; Sestini, *Gazzetta*, 1882, **12**, 292). All these substances differ from the derivative prepared from caramelan in that they represent more highly dehydrated compounds. The composition $C_{24}H_{29}O_{18}Cl_3$ does, however, suggest a chlorinated derivative of the humic acid, $C_{24}H_{22}O_{11}$, which we obtained on hydrolysis with 3 per cent. sulphuric acid (p. 598).

The results therefore obtained on oxidation with nitric acid and with chlorine indicate that the humic acid, $C_{24}H_{22}O_{11}$, is a constant product of the action of acids on caramelan.

(iii) *Forty per Cent. Hydrochloric Acid.*—Cellulose when treated with this reagent for a short time dissolves, and is stated to be converted quantitatively into dextrose (Willstätter, *loc. cit.*). Sucrose, again, gives high yields of ω-chloromethylfurfuraldehyde

(Fischer, *Ber.*, 1914, **47**, 973), this substance being produced entirely from the lævulose formed in the initial hydrolysis. It was thought therefore not unlikely that caramelan would yield one or other of these substances, but quite contrary results were obtained.

Five grams of caramelan were shaken with 50 c.c. of acid of D 1·2. The caramelan did not dissolve, but darkened, and, on keeping, the mixture set to a stiff, black, homogeneous jelly which filled the whole liquid space. The black substance was broken into small pieces and washed with water until free from acid. After drying at 100° it was insoluble in alkali hydroxides and resembled caramelin in appearance. It was not fusible:

0·1226 gave 0·2496 CO_2 and 0·0546 H_2O. C=55·5; H=5·0.

$C_{24}H_{26}O_{13}$ requires C=55·2; H=5·0 per cent.

Caramelan is thus converted into a product having the appearance, composition, and general properties of caramelin (see p. 591). The action of 40 per cent. hydrochloric acid is therefore not one of hydrolysis, as with cellulose and sucrose, but of dehydration, and may be compared with the action of concentrated sulphuric acid on sucrose.

The following scheme contains a summary of the various actions of acids on caramelan described above:
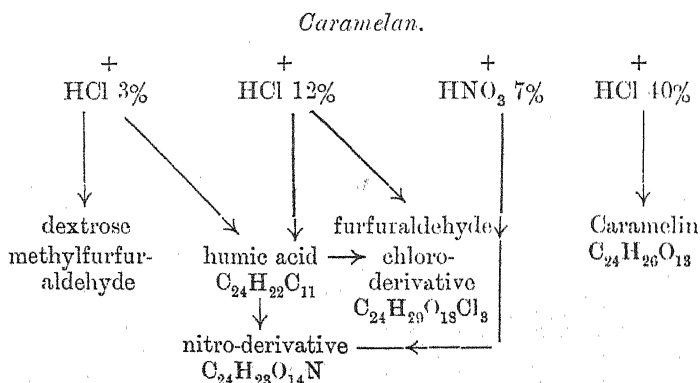
<center>*Caramelan.*</center>

<center>*Acetolysis of Caramelan.*</center>

The use of a reagent consisting of acetic anhydride in the presence of a strong acid has proved of great value in the examination of complex carbohydrates (Skraup, *Monatsh.*, 1901, **22**, 1011). Resolution by the acid and acetylation of the products takes place simultaneously, the simple derived product being isolated as an acetyl derivative. Cellulose, for example,

ultimately gives cellobiose octa-acetate; starch with acetic anhydride saturated with hydrochloric acid gives a chloroacetyl erythrodextrin, and cellulose a hepta-acetyl chlorocellose (Skraup, *ibid.*, 1905, **26**, 1415). Born and Nelson (*J. Amer. Chem. Soc.*, 1915, **54**, 1763) have shown that acetolysis sometimes stops at a monosaccharide and sometimes at a disaccharide, and consider that this is due to the nature of the oxygen linkings connecting the monosaccharide residues. Thus, whilst sucrose gives aceto-bromoglucose, maltose under the same conditions gives aceto-bromomaltose.

Caramelan, therefore, might be expected to give either a monose or a biose, but the results obtained were quite different. Ten grams of dry caramelan were treated with 55 grams of a reagent made by saturating acetic anhydride with dry hydrochloric acid at $-8°$. The mixture, after remaining for ten days at the ordinary temperature, was poured into water, and gave a dark brown, friable solid. This was extracted with benzene, and the filtrate, on cooling, deposited almost white flocks. These were purified by solution in alcohol, and obtained as an almost white powder melting at 107°. In melting point and solubility this substance agrees with caramelan tetra-acetate, the identity with which was confirmed by analysis:

0·1010 gave 0·1877 CO_2 and 0·0509 H_2O. C=50·7; H=5·6.

$C_{20}H_{26}O_{13}$ requires C=50·6; H=5·5 per cent.

The portion insoluble in benzene was left as a black solid, partly soluble in acetone or alcohol. It closely resembled the dehydrated, humus-like products previously described, and on treatment with dilute nitric acid gave a similar red nitro-compound.

The effect of acetolysis under these conditions is thus partly to dehydrate and partly to acetylate the caramelan molecule.

The Action of Oxidising Agents on Caramelan.

Although sensitive to most oxidising agents, caramelan was not found to be resolved into simpler substances which would throw light on its constitution. Potassium permanganate or chromic acid under various conditions gave complex colloidal acid products, soluble only in water, which could not be purified. The action of dilute nitric acid gave unusual results. The actions of bromine water and of ozone have also been investigated.

(1) *Dilute Nitric Acid.*—One hundred grams of caramelan were warmed on the water-bath with 400 c.c. of 7 per cent. nitric acid. The solution, which at first was dark red and opaque, after about thirty minutes became transparent and of a light red colour. Considerable evolution of carbon dioxide and nitrous fumes took

place, and a red, insoluble substance, C, separated which was identical in all its properties with those of the product obtained from the humic acid previously described (p. 599).

Analyses were made (i) of the original substance and (ii) of the precipitate obtained by acidifying its alkaline solution:

(i) 0·01216 gave 0·2296 CO_2 and 0·0518 H_2O. $C=51·3$; $H=4·7$.
   0·3722   ,,   9·5 c.c. N_2 (moist) at 15° and 758 mm. $N=2·9$.

(ii) 0·1882 gave 0·3544 CO_2 and 0·0842 H_2O. $C=51·3$; $H=4·4$.
   0·1450   ,,   3·4 c.c. N_2 (moist) at 16° and 763 mm. $N=2·7$.

$C_{23}H_{23}O_{14}N$ requires $C=51·4$; $H=4·3$; $N=2·6$ per cent.

The substance is therefore not changed by solution in alkali, and its composition suggests that nitric acid, besides oxidising caramelan, has also a nitrating and a dehydrating action. A compound, $C_{23}H_{23}O_{14}N$, would be the nitro-derivative of an acid, $C_{23}H_{24}O_{12}$ (see p. 606). It is probably similar to the yellow acid products obtained by treating coal with nitric acid (*Chem. News*, 1881, **44**, 185).

Examination of the Soluble Products—Filtrate D.

The filtrate from the insoluble compound C was evaporated with water until free from nitric acid. A syrup remained entirely soluble in alcohol, and therefore free from unchanged caramelan. It could not be obtained solid even after long drying in a vacuum. The aqueous solution was strongly acid, reduced silver nitrate and Fehling's solution, and reacted with phenylhydrazine, indicating the presence of a ketonic acid. The syrup was dissolved in water, and (a) one-half of the solution was neutralised with calcium carbonate and (b) the other half treated with phenylhydrazine, which gave an insoluble derivative.

(a) The *calcium* salt of the acid was very readily soluble in water. Alcohol was added to the solution, when a colloidal precipitate was obtained. This was washed with alcohol and dried in a vacuum. It formed a pale brown powder which apparently contained water of crystallisation, but this could not be estimated, since even on warming at 60° the salt decomposed:

0·1080 gave 0·1172 CO_2 and 0·0454 H_2O. $C=29·5$; $H=4·7$.
0·1676   ,,   4·1 c.c. N_2 (moist) at 17° and 758 mm. $N=2·9$.
0·2206   ,,   0·0294 CaO. $Ca=9·5$.

$C_{11}H_{13}O_{10}NCa,5H_2O$ requires $C=29·4$; $H=5·1$; $N=3·2$; $Ca=8·9$ per cent.

That this formula is not improbable will be shown under (b), so that the calcium salt appears to be derived from a nitrated acid, $C_{11}H_{15}O_{10}N$. This acid is probably dibasic, and the reducing

properties of the calcium salt indicate that it contains a ketonic group. An acid, $C_{11}H_{15}O_{10}N$, might be formed from caramelan, $C_{12}H_{18}O_9$, as follows: (1) $C_{12}H_{18}O_9 = C_{12}H_{16}O_8 + H_2O$;

$\qquad$ (2) $C_{12}H_{16}O_8 + HNO_3 + O_2 = C_{11}H_{15}O_{10}N + H_2O + CO_2$.
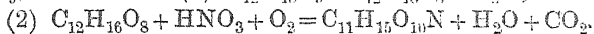
In all cases of oxidation so far investigated, the loss of one carbon atom has been observed, and this seems generally true of the action of oxidising agents on caramelan.

(*b*) The portion of the residue treated with phenylhydrazine in acetic acid solution was warmed on the water-bath for about twenty minutes, when a colloidal precipitate formed which settled after the addition of brine. After being washed with water and dried in a vacuum, it formed a dark red, infusible powder:

$\qquad$ 0·0990 gave 0·1800 CO_2 and 0·0451 H_2O. C = 49·5; H = 5·1.

$\qquad$ 0·1263 ,, 10·8 c.c. N_2 (moist) at 15° and 758 mm. N = 10·0.

$\qquad$ $C_{17}H_{21}O_9N_3$ requires C = 49·6; H = 5·1; N = 10·2 per cent.

These figures are in good agreement with those given for the calcium salt of the acid, $C_{11}H_{15}O_{10}N$, described above. The hydrazone of this acid would be formed directly:

$\qquad$ $C_{11}H_{15}O_{10}N + C_6H_5 \cdot NH \cdot NH_2 = C_{17}H_{21}O_9N_3 + H_2O$.
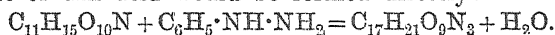
(2) *Nitric Acid* (20 *per cent.*).—With 20 per cent. nitric acid oxidation took place immediately on warming on the water-bath, and the solution, which was at first dark red and opaque, quickly became clear. Considerable evolution of carbon. dioxide and nitrous fumes took place. No insoluble precipitate was formed in this case, and it was noticed during the oxidation of the humic acid, $C_{24}H_{22}O_{11}$, that the red compound, $C_{23}H_{23}O_{14}N$, passed into solution if treatment with the 7 per cent. nitric acid was continued too long. The clear, pale red solution was neutralised with calcium carbonate, and, after concentration, a syrup was obtained which had powerful reducing properties. As no insoluble salt could be obtained from the syrup, the acid was isolated by means of its phenylhydrazine derivative prepared in actic acid solution. The compound, after drying in a vacuum, formed a dark red, infusible powder:

$\qquad$ 0·0892 gave 0·1977 CO_2 and 0·0474 H_2O. C = 60·4; H = 5·9.

$\qquad$ 0·1337 ,, 9·4 c.c. N_2 (moist) at 19·5° and 765 mm. N = 8·1.

$\qquad$ $C_{35}H_{38}O_{11}N_4$ requires C = 60·8; H = 5·5; N = 8·1 per cent.

The composition $C_{35}H_{38}O_{11}N_4$ indicates an acid containing two ketonic groupings and having the composition $C_{23}H_{26}O_{13}$.

$\qquad$ $C_{23}H_{26}O_{13} + 2C_6H_5 \cdot NH \cdot NH_2 = C_{35}H_{38}O_{11}N_4 + 2H_2O$.
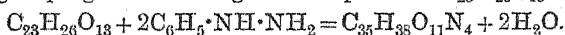
As previously mentioned, the insoluble compound, $C_{23}H_{23}O_{14}N$, was not formed, so that it was probably acted on by the 20 per cent. nitric acid employed. This compound if denitrated would

give an acid, $C_{23}H_{24}O_{12}$, which on further hydrolysis would become $C_{23}H_{26}O_{13}$, and might give the phenylhydrazone, $C_{35}H_{38}O_{11}N_4$, described.

The connexion between these products is shown in the following scheme:

$$C_{24}H_{22}O_{11} \longrightarrow C_{28}H_{23}O_{12}{\cdot}NO_2 + C_{11}H_{15}O_8{\cdot}NO_2$$
(humic acid)   (insoluble acid)   (soluble acid)

$$[C_{23}H_{24}O_{12}]$$

$C_{12}H_{18}O_9$ $\quad+7\%\ HNO_3\quad +30\%\ HNO_3$

$$\longrightarrow [C_{23}H_{26}O_{13}] \quad \text{(isolated as dihydrazone)}$$
(soluble acid)
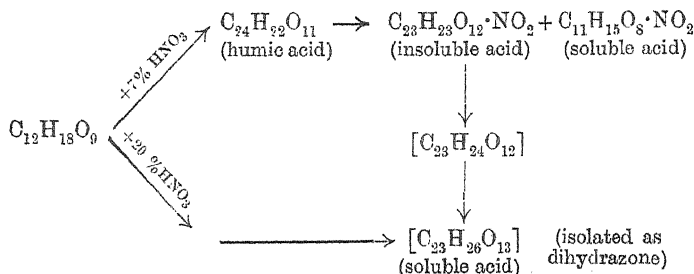
Oxidation with Bromine Water.—The action of this reagent followed the same general lines as oxidation with nitric acid. Complicated bromo-derivatives were obtained, indicating a condensation of molecules and the loss of one carbon atom by oxidation. Two compounds were isolated, namely, $C_{35}H_{53}O_{29}Br$ and $C_{35}H_{52}O_{29}Br_2$. These appear to be bromine substitution products, and are somewhat similar to the sesquibromo-oxysacchulmide, $C_{44}H_{36}O_{22}Br_6$, obtained from sacchulmic acid (Sestini, *Gazzetta*, 1880, **10**, 355).

Bromine water was gradually added to an aqueous solution of caramelan, when the bromine was rapidly absorbed. The solution was poured into alcohol, when a yellow precipitate was obtained. This was collected, washed with alcohol, and dried in a vacuum. It formed a yellow, infusible powder soluble in water, but insoluble in other solvents. The bromine was estimated by boiling with nitric acid in the presence of silver nitrate:

(i) 0·1050 gave 0·0191 AgBr. Br = 7·74.
(ii) 0·1012 ,, 0·0190 AgBr. Br = 7·98.

$C_{35}H_{53}O_{29}Br$ requires Br = 7·9 per cent.

Another experiment was carried out in which, roughly, twice as much bromine water was used, so that the bromine remained in excess. A yellow precipitate was obtained on addition of alcohol:

(1) 0·1306 gave 0·1830 CO_2 and 0·0563 H_2O. C = 38·2; H = 4·8.
0·1156 ,, 0·0398 AgBr. Br = 14·7.
(2) 0·1018 ,, 0·1418 CO_2 and 0·0433 H_2O. C = 38·0; H = 4·7.
0·2187 ,, 0·0753 AgBr. Br = 14·6.

$C_{35}H_{52}O_{29}Br_2$ requires C = 38·2; H = 4·7; Br = 14·6 per cent.

Oxidation with Ozone.—Many experiments were carried out on

the oxidation of caramelan with permanganate and chromic acid, but in each case complex acids, soluble in water, were produced which formed colloidal salts with the manganese and chromium and gave no useful results. Oxidation with ozone was tried in the hope that some cleavage of the molecule might take place which could be interpreted in the light of recent work on the action of ozone. A solution containing 10 grams of caramelan in 100 c.c. of water which, except in thin layers, is opaque, became clear and very pale yellow after four hours' treatment with 2 per cent. ozone. This indicated that some action affecting the caramelan molecule as a whole had taken place, although the weight of ozone reacting could only be small (about 0·5 gram O_3). The formation of an unstable peroxide is the most probable explanation, since on boiling the solution the dark colour returns, and the peroxide appears largely to revert to caramelan. A second treatment with ozone gave the same results. The liquid was strongly acid and gave a precipitate with lead acetate, from which an amorphous, brown-coloured acid was isolated by treatment with hydrogen sulphide. Another portion of the ozonised solution gave an aqueous distillate which contained acetaldehyde in appreciable quantity. This substance was recognised by the usual tests, and, in addition, converted into ethylidenedi-β-naphthol oxide, which gave the correct melting point (173°).

The formation of acetaldehyde from caramelan seems to require the presence of a methyl group in the molecule. This aldehyde would normally be formed from an unsaturated organic compound, $CH_3·CH:CX$, the ozonide of which would be decomposed by water into $CH_3·CHO + X·CO_2H$.

This observation may be of importance, since the recognition of a simple product of decomposition has often been useful in indicating the constitution of organic compounds.

Summary and Conclusions.

(1) Sucrose, on heating at 170—180°, loses 2 molecules of water, forming caramelan, $C_{12}H_{18}O_9$, a tetra-atomic alcohol (m. p. 136°), characterised by the formation of a tetra-acetate (m. p. 107°), a tetrabenzoate (m. p. 105°), and a tetranitrate (explosive). It is not possible to decide definitely between the molecular formulæ $C_{12}H_{18}O_9$ or $C_{24}H_{36}O_{18}$, but the reactions lend some support to the latter.

(2) Compounds formed by caramelan with phenylhydrazine and semicarbazide indicate the existence of one CO- or CHO-grouping

per C_{24} unit, but in each case these are formed with extensive dehydration.

(3) Concentrated non-oxidising acids bring about dehydration to caramelin, $C_{24}H_{26}O_{13}$. Weaker solutions hydrolyse and dehydrate, producing dextrose, methylfurfuraldehyde, and humic acid.

(4) On oxidation, caramelan tends to yield still more complex substances, and in nearly all cases one carbon atom is removed per C_{24} unit. With dilute nitric acid, characteristic nitro-acids are formed. Among simpler products, acetaldehyde has been recognised.

(5) Considered together with the products formed by its further dehydration, caramelan seems to mark a first step in the process of anhydride-formation and condensation which leads from simple sugars to such complex substances as cellulose, humus, and caramelin.

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LIV.—*Action of Acetaldehydeammonia on Quinones.*

By PRAPHULLA CHANDRA GHOSH.

THIS work was undertaken with the object of preparing organic compounds with two quinonoid arrangements in the molecule, and hence dyes of good shade, by introducing one or more auxochrome groups into them. The special reactivity of benzoquinone is well known, so it was thought that it might condense with acetaldehyde-ammonia in molecular proportions and give rise to an anthracene derivative.
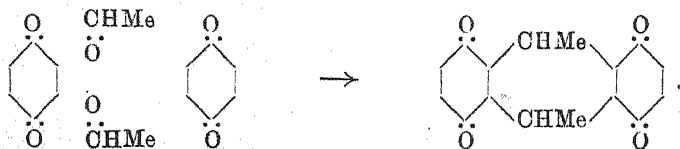
Ammonia liberated from aldehyde-ammonia might react further and form
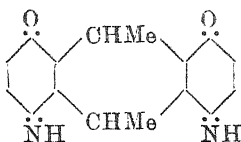
or it might condense as follows to an acridine derivative,

Japp investigated the action of benzaldehyde and aqueous ammonia on quinones (T., 1881, **39**, 225; 1882, **41**, 157), and formulated a somewhat general principle that ortho-quinones are different in constitution from para-quinones, inasmuch as the former condense and the latter do not. The para-quinones investigated by him were benzoquinone and α-naphthaquinone. It is well known, however, that aqueous ammonia resinifies benzoquinone, so it was thought interesting to ascertain whether any conclusion could be drawn as to the constitutional difference between the ortho- and para-quinones by means of the aldehyde-ammonia reaction. Japp himself tried the action of acetaldehyde-ammonia on phenanthraquinone and obtained an amorphous product.
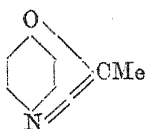
By the condensation of p-benzoquinone and acetaldehyde-ammonia, a deep black, crystalline substance of the formula C_8H_7ON has been obtained. This at once excludes the possibility of any acridine formation; it may, however, have the constitution

if benzoquinone has reacted in the same way as phenanthraquinone does with benzaldehyde and ammonia. A compound of this nature should on oxidation give benzoquinone, whereas on oxidation with chromic acid mixture no benzoquinone, but an amorphous product, was obtained. There is, however, the third possibility, namely, that the compound may be an anthracene derivative. In that case it should have double the empirical formula, but the molecular weight of the substance could not be

determined on account of its sparing solubility. The molecular weight of the nitro-derivative in ethyl alcohol was determined by the ebullioscopic method, and corresponded with the formula $C_{16}H_{12}O_6N_4$. The nitro-derivative therefore has the formula I and the parent substance the formula II.

(I.)   (II.)
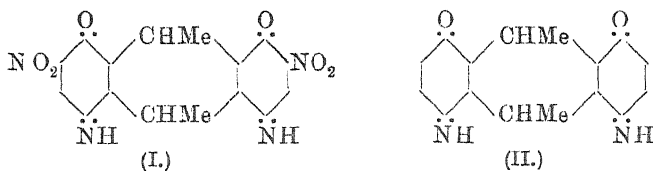
This formula explains the deep colour of the substance, but no known anthracene derivative could be isolated from it. It is, however, difficult to explain the yellow colour of the nitro-derivative on this assumption. Of course, it can be explained by the remarkable conception of the "colour of the secondary order," but the conception is only a very recent one and cannot be said to be thoroughly established. It may be that the substance is more complex, and what is termed the nitro-derivative is only a degradation product, so the constitutional formula suggested is only a probable one and remains undecided at present.

Attempts to prepare the sulphonic acid and other derivatives of the substance were unsuccessful.

With α- and β-naphthaquinones no definite product could be isolated, but with anthraquinone a colourless compound of the formula $C_{18}H_{12}O_2$ was obtained, which on treatment with phenyl-hydrazine in acetic acid solution gave a hydrazone,

$$C_{18}H_{12}(:N \cdot NHPh)_2.$$
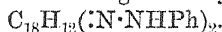
It has, therefore, the constitution
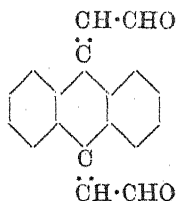
In this condensation of anthraquinone and acetaldehyde, ammonia has probably acted as the condensing agent, and, of course, many such cases are known (compare T., 1883, **43**, 27; *Annalen*, 1894, **281**, 25).

That benzoquinone and anthraquinone condense with acet-aldehyde-ammonia seems somewhat contrary to Japp's generalisation. They differ in their modes of condensation, as there are

reactive hydrogen atoms in benzoquinone but none in anthraquinone.

<div align="center">EXPERIMENTAL.</div>

Condensation of p-Benzoquinone with Acetaldehyde-ammonia.

A nitrobenzene solution of 4·32 grams of *p*-benzoquinone and 2·44 grams of powdered acetaldehyde-ammonia was heated on the oil-bath. There was a sudden solidification at 85—90°. The black mass was then collected and washed free from nitrobenzene with ether, and finally with hot water and alcohol, to free it from unchanged quinone and aldehyde-ammonia. It crystallised from nitrobenzene in deep black needles which did not melt at 290°. It is insoluble in alcohol, chloroform, benzene, or light petroleum, and sparingly soluble in acetic acid, pyridine, or nitrobenzene:

0·1200 gave 0·3181 CO_2 and 0·0507 H_2O. C = 72·3; H = 4·69.

0·1338 ,, 12·25 c.c. N_2 at 25° and 761 mm. N = 10·46.

C_8H_7ON requires C = 72·73; H = 4·55; N = 10·6 per cent.

When *p*-benzoquinone and aldehyde-ammonia were condensed in the proportion of 2 : 1 the same substance was obtained.

Nitro-derivative.—One gram of the finely powdered substance was added gradually to 15 c.c. of nitric acid (D 1·45) without allowing the temperature to rise. After five hours, water was added to the clear solution, when a small quantity of a substance was precipitated. This was collected and the filtrate was concentrated under diminished pressure at 37—42°, when yellow crystals began to appear which did not melt at 300°:

0·125 gave 0·2463 CO_2 and 0·0383 H_2O. C = 53·80; H = 3·41.

0·101 ,, 14·3 c.c. N_2 at 28·5° and 759 mm. N = 16·1.

0·625 in 20 c.c. alcohol gave $\Delta t = +0·17°$. M.W. = 347.

$C_{16}H_{12}O_6N_4$ requires C = 53·93; H = 3·37; N = 15·87 per cent.

<div align="center">M.W. = 356.</div>

Action of Acetaldehyde-ammonia on Anthraquinone.

Anthraquinone (2·08 grams) and acetaldehyde-ammonia (1·22 grams) were heated in a sealed tube at 220—225° for six hours. The product was first washed twice or thrice with cold alcohol to free it from resinous matter as far as practicable, and then boiled with alcohol. The filtrate, on cooling, deposited colourless, silky needles, which when recrystallised from alcohol melted at 281° and contained no nitrogen:

0·11 gave 0·336 CO_2 and 0·049 H_2O. C = 83·1; H = 4·9.

$C_{18}H_{12}O_2$ requires C = 83·07; H = 4·61 per cent.

Hydrazone.—To an acetic acid solution of 0·25 gram of the

substance 0·216 gram of phenylhydrazine was added, and the solution heated on the water-bath for an hour and a-half. Water was then added to the solution, and the yellow precipitate was crystallised from alcohol. The substance did not melt at 300°:

0·102 gave 11·4 c.c. N_2 at 30° and 762 mm.   N = 12·8.

$C_{30}H_{24}N_4$ requires N = 12·72 per cent.

In conclusion, I beg to express my best thanks to Dr. E. R. Watson for the kind help and encouragement which he has given me during the course of this investigation.

DACCA COLLEGE LABORATORY,
      DACCA, BENGAL,
            INDIA.   [*Received, May 25th, 1917.*]

LV.—*The Conversion of* o-*Nitroamines into* isoOxadiazole Oxides, and of o-Nitrosoamines into isoOxadiazoles.

By ARTHUR G. GREEN and FREDERICK MAURICE ROWE.

IN the three previous communications (T., 1912, **101**, 2452; 1913, **103**, 897, 2023) it has been shown that many *o*-nitroamines are converted into furoxans (furazan oxides or *iso*oxadiazole oxides) when oxidised in alkaline solution with sodium hypochlorite. The reaction is undoubtedly a quinonoid one (compare Green and Rowe, T., 1913, **103**, 508), taking place according to the scheme:
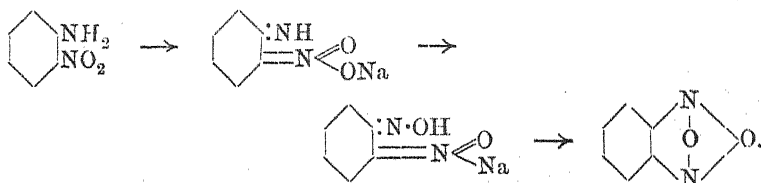
In order further to test the generality of this reaction, the behaviour of *o*-nitroamines of the naphthalene series has been investigated.

The following nitronaphthylamines were submitted to the sodium hypochlorite oxidation:
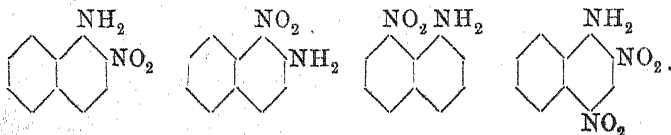
It was found that the same oxidation product is formed both from 2-nitro-1-naphthylamine and from 1-nitro-2-naphthylamine, namely, naphthafuroxan or naphth*iso*ooxadiazole oxide, melting at 127° (identical with the "β-naphthaquinonedioxime peroxide" of Forster and Fierz, T., 1907, **91**, 1942, obtained by heating either 2-nitro-1-naphthylazoimide or 1-nitro-2-naphthylazoimide, and also identical with Koreff and Ilinski's "1:2-dinitrosonaphthalene," formed by oxidation of β-naphthaquinonedioxime). Both preparations of naphthafuroxan are reduced by hydroxylamine to β-naphthaquinonedioxime, which is readily converted into naphthafurazan melting at 78°. This result, coupled with our former observations in the benzene series, and with those of Forster and Fierz (*loc. cit.*) and Forster and Barker (T., 1913, **103**, 1918), place beyond doubt the symmetrical structure of these compounds. Angeli (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 7; *Gazzetta*, 1916, **46**, ii, 300) also confirms the symmetrical structure advanced by us, and simultaneously by Forster and Barker, from results which he has obtained in the fatty series by the action of Grignard's reagent on the peroxide of diphenylglyoxime and anisylmethylglyoxime.

8-Nitro-1-naphthylamine, when subjected to hypochlorite oxidation, did not yield a furoxan. Forster and Fierz also failed to obtain a *peri*-compound by heating the corresponding nitroazoimide. This difference between *peri*- and *ortho*-compounds is similar to that observed in the quinone formation, and, taken in conjunction with the well-known tendency of *peri*-compounds to ring condensation, lends further support to the view that the reaction is a quinonoid one.

With regard to 2:4-dinitronaphthylamine, it was thought possible that this would behave in an analogous manner to 2:4-dinitroaniline. It was found, in fact, that oxidation, either in suspension or in alcoholic solution, at the ordinary temperature or when cooled in ice, resulted in disruption of the ring, accompanied by a strong odour of chloropicrin, and nothing could be isolated from the solution.

This further bears out our previous observations that the amino-, acetylamino-, azo-, sulphonic, and nitro-groups (except in the case of dinitroaniline in alcoholic solution), when occupying the para-position with respect to the amino-group in a ring-substituted *o*-nitroamine, renders the ring unstable to hypochlorite oxidation. This instability is even more pronounced in the naphthalene series than in the benzene series.

The behaviour of *o*-nitrosoamines when oxidised with sodium

hypochlorite was next studied with the object of throwing further light on the mechanism of the formation of furoxans.

Ilinski (*Ber.*, 1886, **19**, 347) obtained the "anhydride of *o*-naphthalenedioxime" (naphthafurazan) by the oxidation of α-nitroso-β-naphthylamine in alkaline solution with potassium ferricyanide. This product was identical with that obtained by Harden (*Annalen*, 1889, **255**, 156) by a similar oxidation of β-nitroso-α-naphthylamine.

We have found that on oxidation with hypochlorite, both α-nitroso-β-naphthylamine and β-nitroso-α-naphthylamine are similarly converted into the same naphthafurazan:

NOH
=NH　or　NH
=NOH →

NOH
=NOH →
N——O
N
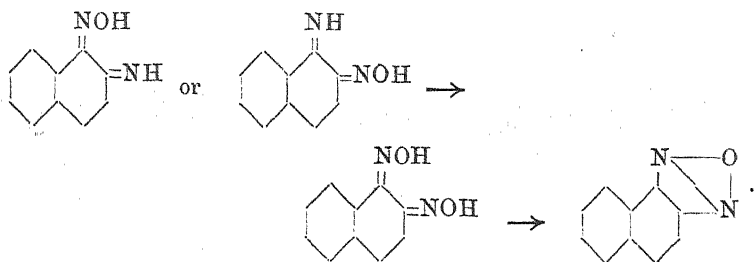
In order to establish the generality of this reaction and its analogy to the hypochlorite oxidation of *o*-nitroamines, we have endeavoured to extend it to the benzene series. A difficulty, however, arises here from the fact that benzenoid *o*-nitrosoamines are not readily obtainable and have only been described in one or two cases, of which only one, namely, *o*-nitrosoacetanilide, was suitable for our purpose. This compound was prepared in a yield of 30 to 50 per cent. by Brand and Stohr (*Ber.*, 1906, **39**, 4064) by the cathodic reduction of *o*-nitroacetanilide in neutral solution followed by oxidation of the hydroxylamine formed with silver nitrate, copper sulphate, or ferric chloride in the presence of sodium acetate.

We have obtained it more conveniently by employing a modification of this method, in which *o*-nitroacetanilide in aqueous suspension is reduced with zinc dust and ammonium chloride, followed by oxidation of the solution of *o*-acetylaminophenyl-hydroxylamine with ferric chloride in the presence of sodium acetate. Attempts to prepare *o*-nitrosoaniline from *o*-nitroso-acetanilide met with no success, this being in agreement with Brand and Stohr's observations, for even boiling with dilute alcohol converts *o*-nitrosoacetanilide into 2:2'-azoxyacetanilide. We also failed to obtain *o*-nitrosoaniline by subjecting *o*-nitro-aniline to reduction and oxidation in a similar manner to the above. The product separates in dull red, crystalline needles,

which proved to be the acetate of a base melting above 310°, the constitution of which was not determined. In the absence of o-nitrosoaniline, we have subjected o-nitrosoacetanilide to hypochlorite oxidation in alkaline solution in the expectation that hydrolysis of the acetyl group and oxidation would occur simultaneously. This was found to be the case, and a quantitative yield of benzfurazan melting at 55° was obtained. In an analogous manner, o-nitroacetanilide was found to be converted directly into benzfuroxan by alkaline hypochlorite.

We next attempted to prepare m-nitrosoaceto-p-toluidide from m-nitroaceto-p-toluidide by the same method as that used for the preparation of o-nitrosoacetanilide. The solution of 6-acetyl-amino-3-tolylhydroxylamine obtained by the reduction of m-nitro-aceto-p-toluidide gave, however, no trace of a nitroso-compound when oxidised with ferric chloride in the presence of sodium acetate. In the absence of sodium acetate, the nitroso-compound was obtained in minute quantity, but attempts to isolate it in a pure condition failed. In spite of numerous experiments carried out under a variety of conditions, only traces of the nitroso-compound were obtained. By distilling the crude product with alkaline sodium hypochlorite in a current of steam, the tolufurazan melting at 37° was obtained in small quantity. This reaction, in fact, affords a convenient test for the presence of an o-nitrosoamine or its acetyl derivative in a mixture. Similarly to o-nitro-acetanilide, m-nitroaceto-p-toluidide when warmed with alkaline sodium hypochlorite is converted into tolufuroxan melting at 97°.

Other attempts to prepare a derivative of m-nitroso-p-toluidide met with no success. Both aceto-p-toluidide and toluene-4-o-tolyl-sulphonamide were subjected to the usual methods of nitrosating, but without any action taking place.

The production of furazans, and not of furoxans (furazan oxides) by the sodium hypochlorite oxidation of o-nitrosoamines is in agreement with our former observations on the resistance of furazans to oxidation (no method is known by which these can be converted into the corresponding oxides). Further support is also given to our explanation of the course of the reaction by which furoxans are formed from o-nitroamines, according to which no transference of an oxygen atom from the nitro-group takes place. The proof is also afforded that in a nitrosoamine (quinoneimide-oxime) the NH_2- (or NH) group is more prone to attack by alkaline oxidising agents than the nitroso- (or oxime) group.

EXPERIMENTAL.

Naphthisooxadiazole Oxide (Naphthafuroxan, "β-Naphtha-quinonedioxime Peroxide," or "1:2-Dinitrosonaphthalene").
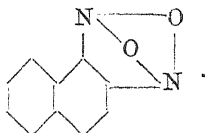
(1) *Preparation from* 1-*Nitro-β-naphthylamine.*—This base was prepared according to the methods of Liebermann and Jacobsen (*Annalen*, 1882, **211**, 45) and Meldola (T., 1885, **47**, 520). Aceto-β-naphthalide (m. p. 132°) was nitrated in acetic acid solution, followed by hydrolysis of the product with sulphuric acid. When crystallised from dilute alcohol, it was obtained in orange needles melting at 124°. The oxidation is best effected by the addition of alkaline sodium hypochlorite to a warm alcoholic solution of the nitronaphthylamine until an excess of hypochlorite is shown by starch iodide paper. The mixture is cooled, diluted with water, the pale yellow precipitate collected, and distilled in a current of steam. When crystallised from alcohol, naphtha-furoxan forms colourless needles melting at 127°, as stated by Koreff, Ilinski, and Forster and Fierz.

The compound has the peculiar pungent odour characteristic of the furoxans. Almost a theoretical yield was obtained. (Found, $N = 14.92$. Calc., $N = 15.05$ per cent.)

(2) *Preparation from* 2-*Nitro-α-naphthylamine.*—This base was obtained by Lellmann and Remy's method (*Ber.*, 1886, **19**, 797; 1887, **20**, 892). Aceto-α-naphthalide (m. p. 158°) was nitrated in acetic acid solution. The crystalline double compound of 2-nitro- and 4-nitro-aceto-α-naphthalide (m. p. 171°) was partly hydrolysed with potassium hydroxide, and the 4-nitro-α-naphthylamine removed with sulphuric acid. The 2-nitroaceto-α-naphthalide (m. p. 199°) was hydrolysed with alcoholic hydrochloric acid. When crystallised from alcohol, 2-nitro-α-naphthylamine was obtained in red needles melting at 144°.
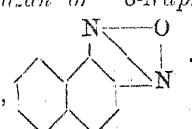
The oxidation with alkaline sodium hypochlorite was effected in alcoholic solution in a similar manner to that employed for the isomeric base. In this case, however, the oxidation product separates as a brown, tarry mass which is best purified by dis-tillation in a current of steam and crystallisation from alcohol. It formed colourless needles melting at 127°, and was completely identical with the preparation from 2-nitro-β-naphthylamine. It

had the same crystalline form, and mixtures of the two products also had the same melting point. A yield of 80 per cent. was obtained. (Found, N = 14·97. Calc., N = 15·05 per cent.)

β-*Naphthaquinonedioxime*,
$$\begin{array}{c} \text{NOH} \\ \text{:NOH.} \end{array}$$
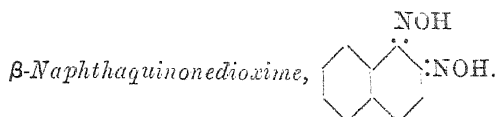
This compound was formed by reduction of the naphthafuroxan prepared from either 1-nitro-β-naphthylamine or 2-nitro-α-naphthylamine. Reduction does not occur as readily as in the benzene series, and requires an excess of hydroxylamine. The best results were obtained by dissolving in alcohol and adding at least four molecular proportions of hydroxylamine hydrochloride in aqueous solution, after which the mixture is warmed to 50°, allowed to remain for some time at that temperature, and then rendered alkaline with aqueous sodium hydroxide. The yellowish-brown solution is cooled, precipitated with acetic acid, the product redissolved in dilute aqueous sodium hydroxide, the solution filtered, and reprecipitated with acetic acid.

The substance separates from alcoholic solution in small, yellow needles melting sharply at 169°. β-Naphthaquinonedioxime is converted into naphthafuroxan on melting, and also by the action of alkalis or acids. This probably accounts for the various melting points which have been given for the compound, namely, Goldschmidt and Schmid, 149° (*Ber.*, 1884, **17**, 2067), Brönner, 166° (*Ber.*, 1888, **21**, 392), Kehrmann and Messinger, 180—181° (*Ber.*, 1890, **23**, 2815). It is interesting to note that whereas the o-quinonedioximes of the benzene series are soluble in alkalis with a deep blood-red colour, β-naphthaquinonedioxime dissolves in alkalis with a yellowish-brown colour. (Found, N = 14·97. Calc., N = 14·89 per cent.)

*Naphth*isooxadiazole (*Naphthafurazan* or "o-*Naphthylene-*

dioxime Anhydride"),
$$\begin{array}{c} \text{N}\text{——O} \\ \text{N} \end{array}$$

(1) *Preparation from β-Naphthaquinonedioxime.*—β-Naphthaquinonedioxime was dissolved in sodium hydroxide and distilled in a current of steam. The product forms long, white, silky needles which melt at 78°. It is readily volatile with steam and possesses the characteristic furazan odour. It is soluble in con-

centrated sulphuric acid with a yellow colour, being precipitated in an unaltered condition on pouring into water. (Found, $N = 16·32$. Calc., $N = 16·47$ per cent.)

(2) *Preparation from α-Nitroso-β-naphthylamine.*—The nitroso-base was prepared according to Ilinski's method (*Ber.*, 1884, **17**, 391; 1886, **19**, 343), by short heating of nitroso-β-naphthol with ammonia at 100°. The product melted at 151°. On addition of sodium hypochlorite to a cold alcoholic solution of nitroso-β-naphthylamine, this base is oxidised quantitatively to naphthafurazan, which is immediately thrown out of solution as a white precipitate. After distillation in a current of steam, it forms long, white, silky needles melting at 78°. (Found, $N = 16·29$. Calc., $N = 16·47$ per cent.)

(3) *Preparation from β-Nitroso-α-naphthylamine.*—The nitroso-base was obtained by Ilinski's method (*Ber.*, 1884, **17**, 2590; 1885, **18**, 706), by heating β-nitroso-α-naphthol (m. p. 148°) with ammonium chloride, ammonium acetate, and ammonium carbonate.

If β-nitroso-α-naphthylamine is oxidised under conditions similar to those used for the isomeric nitroso-base, only a small yield of naphthafurazan is obtained, but by using neutral sodium hypochlorite, it is converted almost quantitatively into naphthafurazan. After distillation in a current of steam, the product formed long, white needles melting at 78°, completely identical with that from α-nitroso-β-naphthylamine. It had the same crystalline form, and mixtures of the two products had the same melting point. (Found, $N = 16·32$. Calc., $N = 16·47$ per cent.)

Benzisooxadiazole (Benzfurazan),
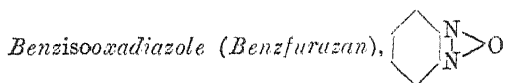
(1) The preparation of this compound, by distilling an alkaline solution of o-benzoquinonedioxime in a current of steam, has already been described in our former paper (*loc. cit.*).

(2) *Preparation from* o-*Nitrosoacetanilide.*—The nitroso-compound was obtained as follows. Twenty-five grams of o-nitroacetanilide were ground to a fine powder and suspended in 350 c.c. of water in which 13 grams of ammonium chloride had been dissolved. Forty grams of zinc dust were then added in small quantities at a time, with cooling and vigorous shaking. Agitation was continued until all the o-nitroacetanilide had disappeared. On filtration, a clear yellow solution of o-acetyl-aminophenylhydroxylamine was obtained. This solution is readily oxidised by air to 2:2'-azoxyacetanilide (yellow needles from

alcohol, m. p. 185°), which doubtless owes its formation to the condensation of *o*-nitrosoacetanilide with *o*-acetylaminodiphenyl-hydroxylamine. Owing to the extreme ease with which this condensation occurs, it is necessary for its avoidance that the oxidation of the *o*-acetylaminodiphenylhydroxylamine solution should take place as rapidly as possible. Further, conditions of alkalinity or mineral acidity must be excluded. The solution of *o*-acetylamino-phenylhydroxylamine was therefore filtered from zinc direct into a cold solution of three to four molecular proportions of ferric chloride containing sufficient sodium acetate to neutralise the mineral acid liberated by the oxidation. A green precipitate, consisting of a mixture of *o*-nitrosoacetanilide and azoxyacetanilide, separated, which was collected and dried. A further quantity could be obtained from the filtrate by extraction with ether or benzene. The *o*-nitrosoacetanilide was extracted from the crude product by ether, and after two crystallisations from ether was obtained in very large, green, rhombic prisms melting at 107·5°.

It may be conveniently estimated by titration with titanous chloride, and was thus found to be 99·75 per cent. (Found, $N = 16·97$. Calc., $N = 17·07$ per cent.)

All attempts to prepare *o*-nitrosoaniline from *o*-nitrosoacetanilide were unsuccessful. The latter dissolves in cold concentrated hydrochloric acid with a deep red colour, which deposits a yellowish-brown, crystalline product melting at 258—262°. This was not the hydrochloride of *o*-nitrosoaniline (m. p. 220°).

The oxidation of *o*-nitrosoacetanilide with sodium hypochlorite was carried out as follows:

Powdered *o*-nitrosoacetanilide was covered with a solution of sodium hypochlorite made strongly alkaline with sodium hydroxide. On warming gently, the *o*-nitrosoacetanilide dissolved with a deep red colour, which was rapidly decolorised, and benzfurazan separated. After distillation in a current of steam, the product crystallised from alcohol in long, white needles melting at 55°, completely identical with the preparation from *o*-benzoquinone-dioxime.

5-Methylbenzisooxadiazole (*Tolufurazan*),
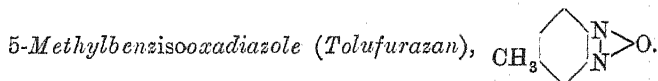
(1) The preparation of this compound, by distilling an alkaline solution of 3:4-toluquinonedioxime in a current of steam, has been described in our former paper (*loc. cit.*).

(2) *m*-Nitroaceto-*p*-toluidide was reduced in aqueous suspension with zinc dust and ammonium chloride, as in the previous pre-

paration of o-nitrosoacetanilide.   The solution of the hydroxyl-amine obtained was oxidised with ferric chloride, but in this case no sodium acetate was used.   The crude oxidation product which separated was mixed with sodium hypochlorite, made alkaline with sodium hydroxide and distilled in a current of steam.   The product crystallised from dilute alcohol in long, white needles melting at 37°, completely identical with the former preparation of 5-methylbenz*iso*oxadiazole.

About 1 gram was obtained from 80 grams of *m*-nitroaceto-*p*-toluidide.

School of Technology,
    Manchester.

LVI.—*The Phosphates of Calcium.   Part IV. The Basic Phosphates.**

By Henry Bassett, jun.

A detailed knowledge of the basic phosphates of calcium is desirable, if only for the reason that they are important constituents of the mineral matter of bone and also of the earthy phosphorites and coprolites so largely used in the manufacture of superphosphate.

It is true that one still finds statements in text-books to the effect that these substances consist of tricalcium phosphate.   This is far from being the case, however.   Even laboratory preparations of so-called tricalcium phosphate vary considerably in composition and seldom have the correct CaO,P_2O_5 ratio.   Cameron, Seidell, and Bell (*J. Amer. Chem. Soc.*, 1905, **27**, 1512), when determining the isotherm of the system $CaO-P_2O_5-H_2O$ at 25°, examined the region of alkaline and very faintly acid solutions, and concluded that no definite compound existed intermediate between $CaHPO_4,2H_2O$ and $Ca(OH)_2$, but only a series of solid solutions.

Cameron and his co-workers have drawn similar conclusions in other cases also, conclusions which always seemed unsound to the present author, and have been shown to be incorrect in the case of calcium nitrate (Bassett and Taylor, T., 1914, **105**, 1926).   The present communication is the result of experiments which have been in progress for a number of years past.   A preliminary account

* The first three parts of this series were published in the *Zeitsch. anorg. Chem.*, 1907, **53**, 34, 49 ; 1908, **59**, 1.

of the conclusions arrived at has already been given (*Proc. 7th Internat. Congress Applied Chem.*, 1909, Sec. II., p. 178), but these have had to be modified somewhat as the result of further experiments.

<div align="center">EXPERIMENTAL.</div>

The plan of the investigation is simple enough, being merely a phase-rule examination of that portion of the system

$$CaO-P_2O_5-H_2O$$
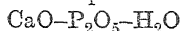
lying between the regions where dicalcium phosphate and calcium hydroxide respectively are the stable solid phases. The experimental difficulties encountered have, however, been serious, and were chiefly due to the extreme slowness with which equilibrium is attained.

The difficulties were also increased by the necessity of using vessels which were unattacked by the solutions employed.

A great deal of time was consumed by preliminary series of experiments designed to determine the approximate nature of the solid phases being dealt with and the time required to reach equilibrium. Most of the experiments have been carried out at 25°, the reacting mixtures being contained in cerasin wax bottles, which were constantly shaken in a thermostat kept at that temperature until it was judged that equilibrium had been attained. Some experiments were also made at 100° and in an autoclave at from 170° to 200°, platinum vessels being employed in these cases. In the case of the experiments at 25°, it has been found that, even in the most favourable circumstances, at least eighteen months are required for equilibrium to be reached. This seems to be due, in the main, to the slowness with which a mixture of two solids [for example, the compounds $Ca(OH)_2$ and $CaHPO_4,2H_2O$] reacts to give the single new solid (for example, $Ca_3P_2O_8$), really stable under the experimental conditions. The solution seems to adjust itself to any single solid when present alone comparatively quickly, even in cases where the solid is only very sparingly soluble. It is the reluctance to form the new compound that delays matters.

When dealing with sparingly soluble compounds, other complications arise. Thus it has been found that basic phosphate mixtures prepared from calcium hydroxide and the compound $CaH_4P_2O_8,H_2O$ would not reach equilibrium in a reasonable time owing, apparently, to some of the former becoming coated over with the compound $CaHPO_4,2H_2O$ or a more insoluble basic phosphate.

If, on the other hand, milk of lime and phosphoric acid were used in making the original mixture, the basic phosphate solid obtained, even after shaking for a year or more, was so amorphous and

C C

settled so badly that it was almost impossible to separate the solution and solid for satisfactory analysis.

If anhydrous calcium hydrogen phosphate, $CaHPO_4$, was used in making the mixtures, it reacted with such extraordinary slowness that some was nearly always present in the final solid phase separated for analysis.

The only way in which approximately satisfactory results have been obtained has been by making up the contents of the solubility bottles with pure lime, pure calcium hydrogen phosphate, $CaHPO_4,2H_2O$, and distilled water. The lime was obtained by the ignition of pure calcium carbonate, precipitated by ammonium carbonate and specially prepared so as to be free from traces of iron, magnesium, etc.* The calcium hydrogen phosphate was also free from such impurities, and was obtained by precipitation with ammonium phosphate of a solution of the pure calcium carbonate in hydrochloric acid. The molecular structure of calcium hydrogen phosphate, $CaHPO_4,2H_2O$, seems to be such that it can take up additional lime with very little disturbance to the crystalline form. This materially facilitates the attainment of equilibrium, and results in the formation of a solid which, although almost certainly amorphous, is crystalline in appearance and general properties, such as the readiness with which it settles and can be washed. In fact, all the basic phosphates prepared in this way appeared under the microscope almost exactly like the original crystals of calcium hydrogen phosphate, of which they were pseudomorphs, and only differed from them in having no action on polarised light. They were often still quite clear and transparent, although sometimes a little cloudy.

Experiments at 25°.

In the case of the experiments at 25°, solid and solution were separated for analysis by filtration in the thermostat approximately in the manner indicated in Part III. (*Zeitsch. anorg. Chem.*, 1908, **59**, 12). The solid phase was washed with a small quantity of alcohol, then with ether, and left exposed to the air for a short time before analysis. In the earlier experiments the loss on ignition was determined and then the lime and phosphoric oxide on the same sample. In later experiments the loss of weight over sulphuric acid in an exhausted desiccator was first determined, followed by loss on ignition and then estimation of the lime and phosphoric oxide. As far as possible, all estimations were made on the same weighed quantity of solid in order to economise material.

* The calcium carbonate so prepared contained 0·008 per cent. of chlorine.

It was necessary to separate the solid phase in the dry state for analysis. Analysis of the wet solids and use of the triangular diagram method would have been of little use for fixing the nature of the solid phases owing to the extreme dilution of the solutions. Owing to the fact that some of the water present in the solids is rather loosely held, it is probable that it has been affected by the washing with alcohol and ether. Apart from that, however, there need be no fear that the composition of the solids has been affected by the treatment. Owing to the amorphous character of the solids, the percentage of water they contain is relatively unimportant— there is no evidence that one is dealing with definite hydrates. In all the experiments dealt with in this paper the concentrations of the equilibrium solutions are so small that the greatest care had to be used in making up the original mixtures in order to get points well spaced over the experimental region. The amount of total solid employed was usually about 2 grams for 100 c.c. of water in each experiment.

This was sufficient for analysis, etc., whilst it was judged that the proportion of solid to solution would be sufficient to keep the latter properly saturated without excessively prolonging the time required for the complete readjustment of the solid.

The experimental results are given in tables I and II, and those for 25° are also represented graphically.

There seems little doubt that, in spite of the length of time allowed, equilibrium had not been fully attained in many cases. It seems as well to discuss the results as they stand, however, for more regular results might not be obtained even if a fresh series of experiments was started and allowed to run for two years or more. The numbers in the first column of table I do not denote the order of the experiments, which belong to several series. They are merely the order in which the points come on the curve, and have only been given for purposes of reference.

Solids 1, 3, 4, and 6 are clearly $CaHPO_4,2H_2O$ ($P_2O_5/CaO =$ 1·267). From 8 to 17 we have a group of solids characterised by a P_2O_5/CaO ratio, which approximates to the value 0·845 of tri-calcium phosphate, and it seems legitimate to conclude that, in the main, these solids do actually consist of that compound. That the P_2O_5/CaO ratios are mostly too high probably means that there is still a small amount of dicalcium phosphate left in the centre of the grains. The time allowed has not been quite suffi-cient for complete penetration of the additional lime required for complete formation of the tricalcium compound.

Position 7 probably represents the point at which the curves of di- and tri-calcium phosphates intersect.

TABLE I.

Solid Phase.

Experi-ment.	Solution.		Per cent. H_2O lost over H_2SO_4.	Per cent. H_2O lost on igni-tion.[1]	Per cent. CaO.	Per cent. P_2O_5.	Per cent. CO_2.	Total.	Per cent. P_2O_5 per cent. CaO.[2]	Remarks.
	Per cent. P_2O_5.	Per cent. CaO.								
1	0·149	0·0617	—	26·13	32·66	41·27	—	100·06	1·264	Solid phase = $CaHPO_4,2H_2O$.
2	·121	0·0507	—	20·63	37·74	40·93	nil	99·30	1·085	Shaken 14 months in silica flask; original mixture made from CaO; $CaHPO_4,2H_2O$ and $CaH_4P_2O_8,H_2O$.
3	0·119	0·0485	—	26·26	32·39	41·10	—	99·75	1·269	Solid phase = $CaHPO_4,2H_2O$.
4	0·108	0·0426	—	26·48	32·00	40·87	—	99·35	1·277	Shaken 4 months in silica flask.
5	0·105	0·0427	—	20·75	37·96	41·11	—	99·82	1·083	Shaken 1 year in silica flask.
6	0·101	0·0428	—	26·66	32·28	40·68	—	99·62	1·260	Solid phase = $CaHPO_4,2H_2O$; 14 months in silica flask.
7	0·0980	0·0406	4·86	18·39	41·46	39·96	nil	99·81	0·964	Made from CaO and $CaH_4P_2O_8,H_2O$; 1 year in silica flask.
8	0·0947	0·0389	—	10·71	47·07	41·28	0·16	99·22	0·877 (0·881)	
9	0·0897	0·0373	—	25·03	33·73	40·69	nil	99·45	1·206	Made from CaO; $CaHPO_4,2H_2O$; $CaH_2P_2O_8,H_2O$; 14 months in silica flask.
10	0·0777	0·0326	—	4·15*	52·54	41·30	0·11	98·10	0·786 (0·788)	H_3PO_4 and oxyapatite pre-pared at 100° (see page 633) used for mixture. Shaken 8 months in silica flask.

No.										Notes
11	0·0727	0·0299	4·37	12·51	47·26	39·96	0·09	99·72	0·846 (0·848)	Shaken 1 year in silica flask.
12	0·0607	0·0269	—	9·58	48·40	40·52	0·12	98·62	0·837 (0·840)	
13	0·0465	0·0191	2·59	16·46	44·10	39·14	0·04	99·70	0·888 (0·889)	Made from CaO; $CaHPO_4,2H_2O$; $CaH_4P_2O_8,H_2O$; 9 months in platinum flask.
14	0·0423	0·0175	1·80	13·79	45·13	40·28	0·09	99·20	0·892 (0·895)	
15	0·0414	0·0174	2·66	13·76	45·62	40·11	nil	99·47	0·879	
16	0·0405	0·0167	2·76	12·66	46·52	40·42	0·09	99·60	0·869 (0·871)	
17	0·0302	0·0122	2·83	9·83	48·88	40·49	0·10	99·20	0·829 (0·831)	
18	0·0196	0·00893	—	8·23*	50·11	39·84	0·12	98·30	0·795 (0·798)	
19	0·0134	0·00582	—	7·86*	50·34	39·58	nil	97·78	0·786	Made from CaO; $CaHPO_4,2H_2O$; $CaH_4P_2O_8,2H_2O$; 14 months in silica flask.
20	0·00613	0·00600	4·47	9·22*	49·87	39·06	0·22	98·15	0·783 (0·783)	13 months in silica flask. Solid phase prepared at 100° (see page 633). Shaken 1 year at 25° in silver flask.
21	0·00575	0·00512	3·94	8·60*	50·01	39·59	0·36	98·20	0·792 (0·799)	
22	0·00238	0·00166	3·33	7·60*	50·86	39·32	0·35	97·78	0·773 (0·781)	
23	0·00043	0·00158	3·30	7·72*	50·95	39·47	0·22	98·14	0·775 (0·779)	
24	0·0001 (?)	0·00146	4·33	8·98*	50·18	38·59	0·60	97·75	0·769 (0·781)	
25	0·0012	0·0058	—	7·77*	50·40	38·66	0·28	97·11	0·767 (0·773)	
26	0·000055	0·0097	—	3·23*	53·21	40·86	0·16	97·46	0·768 (0·771)	

[1] Any water lost over sulphuric acid is included in this figure. Any carbon dioxide found has been deducted from the actual loss on ignition before calculating the percentage loss due to water. An asterisk (*) against figures in this column indicates that the ignited solid had a pink colour.

[2] Figures in brackets in this column have been obtained after deducting line equivalent as calcium carbonate to any carbon dioxide found.

In all the experiments quoted in Table I., unless there is a note to the contrary, cerasin wax bottles were used and the shaking at 25° was continued for from 17 to 19 months.

TABLE I. (continued)

Solid Phase.

Experiment	Solution. Per cent. P₂O₅	Per cent. CaO	Per cent. H₂O lost over H₂SO₄	Per cent. H₂O lost [1] on ignition.	Per cent. CaO.	Per cent. P₂O₅.	Per cent. CO₂.	Total.	Per cent. P₂O₅ [1] per cent. CaO.	Remarks.
27	0·00014	0·0182	—	10·01	50·68	36·28	0·62	97·59	0·716 (0·727)	This solid was examined quantitatively for alkalis, which were found to be absent.
28	0·0001 (?)	0·0612	4·15	10·37*	49·88	37·54	0·69	97·79	0·753 (0·760)	
29	0·00004	0·0939	4·39	10·49*	49·87	37·39	0·67	97·75	0·750 (0·763)	
30	Not enough to detect.	0·1034	—	8·77	50·85	35·57	2·16	97·35	0·700 (0·740)	
31	0·00012 (?)	0·112	4·13	10·54*	49·75	37·49	0·57	97·78	0·755 (0·765)	There was probably far less phosphoric oxide in this solution than the amount indicated. The determination was uncertain.
32	Not enough P₂O₅ to detect in these solutions.	0·1148	—	10·20	52·57	33·93	0·55	97·25	0·645 (0·654)	
33		0·1146	—	10·25	54·11	31·44	1·88	97·68	0·581 (0·608)	The carbon dioxide was determined in these two solids after keeping for 2½ years in well corked tubes. Other figures obtained on fresh solids, which then contained no carbon dioxide
34		0·115	—	11·29	55·57	29·04	1·87	97·77	0·523 (0·546)	
35		0·1141	—	11·13	55·60	28·17	3·37	98·27	0·507 (0·549)	
36		0·114	—	16·56	64·13	18·41	(5·44)	99·10	0·287	
37	nil	0·1159	—	24·41	75·59	nil	(1·82)	100·00	Solid phase Ca(OH)₂	

[1] See footnotes, p. 625.

TABLE II.

Experiment	Solution.		Solid Phase.						Remarks.
	Per cent. P_2O_5.	Per cent. CaO.	Loss on ignition (H_2O+CO_2).	Per cent. CaO.	Per cent. P_2O_5.	Per cent. CO_2.	Total.	Per cent.P_2O_5._____ per cent. CaO.	
Experiments at 100° :—									
1	0·133	0·0474	5·64	47·40	46·35	—	99·39	0·978	Boiled 4 weeks in platinum flask. About half of solid phase seemed to consist of crystals of $CaHPO_4$.
2	0·117	0·0456	4·54*	51·59	42·54	0·03	98·67	0·825	Boiled 9 weeks in platinum flask. The pink colour of ignited solid was very pale and patchy. Boiled 5 weeks in platinum flask.
3	0·115	0·0416	4·97*	51·12	42·93	0·11	99·02	0·840	
4	0·0896	0·0355	4·19*	52·47	41·59	nil	98·25	0·793	Boiled 5 weeks in platinum flask.
5	0·000012	0·00001	3·95*	53·11	40·66	0·14	97·72	0·765	Experiment carried out in special way. See page 632.
6	0·0005	0·0162	3·77*	53·38	40·79	0·33	97·94	0·764	Boiled 3 months in platinum flask.
7 ‖	Not enough to detect.	0·0501	4·62*	52·64	40·13	0·50	97·39	0·762	This solid also contained $SnO_2 =$ 0·3 per cent. A silver flask and tin condenser tube had been used in the experiment. Boiled 6 weeks.
Autoclave experiments :—									
8	0·151	0·0559	5·09	48·58	45·33	—	99·0	0·933	97 hours' heating at 170–180°.
9	0·154	0·0606	3·95	51·26	44·05	0·20	99·26	0·859	39 hours' heating at 190–200°.
10	0·160	0·0660	3·16*	52·33	42·48	0·07	97·97	0·831	35 hours' heating at 190–205°. The pink tinge on the ignited solid was very pale.
11	0·197	0·0885	2·35*	53·21	42·52	0·11	98·08	0·799	26 hours' heating at 200–210°.
12	trace.	trace.	1·84*	54·01	41·17	0·55	97·02	0·762	23 hours' heating at 200–240°.
13	0·0003	0·062	4·59*	55·38	37·68	0·65	97·65	0·681	33 hours' heating at 200–210°.

An asterisk (*) in column 4 indicates that the ignited solid had a pink colour.

Solids 2, 5, and 9 lying on either side of position 7 also appear to be mixtures of di- and tri-calcium phosphates, but 7 belongs to the latest and most trustworthy series of experiments.

Solids 18 to 29 have P_2O_5/CaO ratios which are not very far removed from the 0·761 of oxyapatite, $(Ca_3P_2O_8)_3.CaO$, of which they appear to consist.

Solids 30 to 36 all give the same equilibrium solution, which clearly corresponds with the point at which both oxyapatite and calcium hydroxide can co-exist.

Solids 32 to 36 could be seen to be heterogeneous under the microscope and to contain pseudomorphs of calcium hydrogen phosphate crystals (the oxyapatite) and minute crystals with a marked action on polarised light (the calcium hydroxide).

Point 37 gives the solubility of pure calcium hydroxide at 25°.

It will be noticed that the region of oxyapatite is fairly extensive and reaches very nearly to the point representing the solubility of pure calcium hydroxide. There is no indication whatever of the existence of any compound, such as tetracalcium phosphate, $Ca_4P_2O_9$, more basic than oxyapatite. Nor is there any evidence in support of compounds intermediate between di- and tri-calcium phosphates (compare Buch, *Zeitsch. anorg. Chem.*, 1907, **52**, 323). The experimental results seem to show pretty clearly that Cameron, Seidell, and Bell's assumption (*loc. cit.*) of a series of solid solutions is erroneous, and the interpretation of the data just offered seems adequate and satisfactory.

The Difficulty with which Water is Driven off from some of the Basic Phosphates.

The analyses of the oxyapatite solids always show a large deficit, more than 2 per cent. as a rule. With the exception of one of the tricalcium phosphate solids, which shows a deficit of 1·3 per cent., the other analyses are generally satisfactory.

To what is this deficit to be ascribed? It can scarcely be laid at the door of the method of analysis, which was the same in all cases and was specially tested on pure calcium hydrogen phosphate, with which excellent results were obtained. (Found, $H_2O = 26·30$; $CaO = 32·44$; $P_2O_5 = 40·97$; total, 99·71 per cent. P_2O_5/CaO 1·263.)

The method of analysis adopted as being the quickest and most satisfactory was as follows. The loss on ignition was determined after ten minutes' ignition in a platinum crucible over the blow-pipe. The ignited solid was dissolved in hydrochloric acid and the solution digested for from two to four hours before precipitating the calcium as oxalate; this was to hydrolyse any phosphate, other than orthophosphate, which might be present in the ignited solid.

The calcium oxalate precipitate, after filtering and washing, was dissolved in hot dilute sulphuric acid and titrated with standard permanganate. The phosphoric acid was determined in the calcium oxalate filtrate, being weighed as $Mg_2P_2O_7$ after double precipitation as magnesium ammonium phosphate.

Although specially purified materials had been used in preparing the oxyapatite solids, the latter were examined for possible impurities, but for the most part with negative results. Alkali metals, in particular, were found to be absent.

Most of the basic phosphate solids were found to contain small amounts of carbon dioxide. The absorption of traces of this is almost unavoidable when the mixtures are being made up, but the large amounts found in some of the solids had certainly been absorbed during storage subsequent to separation from the equilibrium solutions.

It is only latterly that carbon dioxide in the solids has been determined and in many cases in solids which had been kept for some time. In such cases the whole analysis was repeated, so that the figures for lime, etc., given in the tables were obtained at the same date as those for carbon dioxide. It is known that many of the solids showing considerable amounts of carbon dioxide originally contained no more than traces. This applies especially to solids 30 and 32 to 36, which had been kept in corked tubes for two and a-half years before the carbon dioxide was determined.

In determining the carbon dioxide the solids were dissolved in concentrated phosphoric acid (1 part of syrupy acid to 1 part of water). The carbon dioxide evolved was carried by a slow current of air free from that gas through a sulphuric acid drying tube into a weighed potash bulb. Gentle heating facilitated solution of the calcium phosphate and also complete expulsion of the carbon dioxide.

Most of the carbon dioxide is driven off by strong ignition of the solid phosphate, and probably in many cases it is expelled completely. Solid 29 before ignition contained $CO_2 = 0.67$ per cent.; after fifteen minutes' ignition over the blow-pipe there was still carbon dioxide present, which amounted to 0.16 per cent. of the original solid.

The total water lost on ignition (column 5 in table I) has been obtained from the total loss on ignition by deducting the carbon dioxide found by the method indicated above.

With the exception of one metal found in traces in some of the solids, and considered later, no other impurities could be found in the basic phosphate solids. The analytical deficit is therefore still unaccounted for, and the only explanation appears to be that it

is due to water held so firmly that it is not driven off even by very strong ignition. Ignition for several hours in the muffle did not expel it. Attempts to estimate this water directly by fusion with lead oxide have not so far been successful, although they have given indications that it is really present. Further experiments on this point will have to be postponed.

It is well known that certain silicate minerals contain water which cannot be expelled by simple ignition, but only after complete destruction of the molecule, as by fusion with lead oxide (see Classen, "Ausgewählte Methoden der analytischen Chemie," 1903, Vol. II., p. 629). Such water is usually called "water of constitution," and, in the case of silicates, is regarded as being associated with the silicic acid. It seems quite likely that some of the water in a compound like oxyapatite may be combined in a similar manner.

It may be mentioned that, according to Gabriel (*Zeitsch. physiol. Chem.*, 1894, **18**, 257), there is more than 1 per cent. of water in bone phosphate which is not driven off on ignition. He states that it can be expelled by strong ignition with silica. Van Bemmelen (*Zeitsch. anorg. Chem.*, 1897, **15**, 90) found some similarly combined water in fossil bone.

The Pink Colour of some of the Ignited Phosphates.

The oxyapatite solids were also peculiar in another respect. The ignited solids nearly always had a pink colour. This varied in intensity with different solids, and in some cases was only very faint. It was generally deepest near the bottom of the crucible, where the temperature would be highest. Very often, too, it was inclined to be patchy and deeper in some portions than others of the ignited solid. The colour was obtained whether the ignition was carried out in a platinum or a porcelain crucible, but only with the solids approximating to oxyapatite in composition. It was a long time before the cause of this pink colour was discovered.

Gabriel (*loc. cit.*) noticed a similar pink colour in bone ash after strong ignition, but was not able to discover the cause. He was unable to confirm a statement of Cossa (*Atti R. Accad. Lincei*, 1878, **3**, 17; *Gazzetta*, 1879, **9**, 118) that traces of ceria earths are present in bone ash. Neither could he impart a pink colour to pure calcium phosphate by addition of cerium salts or of manganese salts.

The present author has also examined bone ash for rare earths with entirely negative results. None could be obtained from a kilogram of bone ash.

The clue to the cause of the pink colour was finally given by the solid from one of the autoclave experiments (Expt. 12, table II). During the analysis of this it was noticed that after ignition the pink colour was particularly deep at certain spots on the top of the solid, as though due to specks fallen from the lid of the autoclave. The hydrochloric acid solution of the ignited solid was nearly neutralised with ammonia and then saturated with hydrogen sulphide. This caused a slight darkening, but no visible precipitate. However, on digestion over a small flame, the few flocks of sulphur which separated were blackish. They were collected and ignited in a clean porcelain crucible. Less than 0·0001 gram of residue remained (this was from 0·2346 gram of original solid), but on treating it with a drop of dilute nitric acid and then one of ammonia (D 0·880), a blue colour was obtained, showing that copper was certainly present. On warming over a very small flame, a pale green tinge was seen on the white porcelain when dryness was reached. There can be no doubt that the pink colour after ignition of the oxyapatite solids is due to some impurity, for its intensity varies a good deal with different preparations. In the case of one series of experiments (30 to 36 and 27), the ignited solids were white.

That the pink colour is probably due to traces of copper in all cases was confirmed by the following experiments:

(a) Some of solid 30 (which, ignited by itself, remains quite white) was moistened with a very dilute solution of copper nitrate dried, and ignited over the Bunsen burner. A pale pink colour had developed, which, after ten minutes' ignition over the blowpipe, became very much deeper—much deeper than the pink colour given by any of the untreated basic phosphate solids, but of the same character.

(b) One of the autoclave solids with P_2O_5/CaO ratio 0·859 (Expt. 9, table II) was similarly ignited after moistening with dilute copper nitrate solution, but was quite white afterwards.

(c) Some of the pure calcium carbonate used in the basic phosphate experiments was similarly treated, but in no case was any pink colour obtained. If only a very small trace of copper nitrate was used, the ignited lime was white, but with more copper salt it had a grey colour.

It seems fair to conclude from these results not only that the pink colour of the ignited oxyapatite solids (and also of strongly ignited bone ash) is due to traces of copper, but also that the presence of the oxyapatite compound is actually necessary for the development of the pink colour. It would seem, indeed, that the development of a pink colour on igniting a calcium phosphate

with a trace of copper nitrate might be regarded as a specific test for the presence of oxyapatite.

It is worth noting that the constant presence of traces of copper in animal tissues has been shown by several investigators (Bergeron and L'Hôte, *Compt. rend.*, 1875, **80**, 268; Raoult and Breton, *ibid.*, 1877, **85**, 40).

It may be pointed out that the pink colour after strong ignition was very faint both in the case of the bone phosphate used in the experiments described on p. 640 and the ox bone from which it was prepared. Some ox bone (rib) recently examined also had only a very pale pink colour after strong ignition, not nearly so marked as that obtained with many of the synthetic basic phosphates.

The author understands that the ash of hops, malt, etc., often has a slight pink colour which has been shown to be due to the presence of traces of copper, and possibly other similar cases are on record.

Experiments at 100° *and Higher Temperatures.*

These were carried out in the hope of obtaining results more rapidly and with less difficulty.

In the experiments at 100°, the solutions were gently boiled in a platinum flask (100 c.c. capacity) provided with a long neck, around which a small condenser was fitted. Entrance of carbon dioxide was prevented by a small soda-lime tube.

The solutions, being all very dilute, boiled practically at 100°, and this method of operating kept the solutions at a constant temperature (the metal flask prevents superheating) and also kept solid and solution well mixed. It was found that at least four weeks' boiling was necessary for the attainment of approximate equilibrium (with about 2 grams of solid and 95 c.c. of solution present). Satisfactory results were only obtained, as at 25°, when the initial mixtures were prepared from calcium hydrogen phosphate, $CaHPO_4,2H_2O$, lime, and water. Expt. 5, table II, was carried out in the following special way, which is possible at 100° owing to the reaction being more rapid at the higher temperature. Although distinctly troublesome, it has advantages, and results can be obtained more quickly than when all the lime is added at the beginning.

A mixture of 1·72 grams of calcium hydrogen phosphate, 0·28 gram of lime, and 25 c.c. of water was boiled for twenty-four hours in the platinum flask. The solution was then acid, and a solution of 0·1 gram of lime in 100 c.c. of water was added in

portions of 10 c.c. at a time at intervals of twenty-four hours. In this way the solution was kept slightly acid after each addition. After the ninth addition it was practically neutral. Then 7 c.c. more of the lime solution were added (93·3 c.c. theoretically needed to form oxyapatite), and the contents of the flask boiled for another two weeks before filtration and analysis. The boiling was continuous during the twenty-five days the experiment lasted, some water being allowed to boil away occasionally, so that the total volume of solution was about 90 c.c. by the time all the lime had been added.

The solids used in experiments 10 and 26 of table I had also been prepared at 100° in the manner just described.

The experiments at higher temperatures than 100° were carried out by heating suitable mixtures in a large platinum crucible in an autoclave to temperatures ranging from 170° to 240°. The total time of heating varied in different experiments from twenty-three to ninety-seven hours. It was not found possible to obtain an autoclave which did not lose water rapidly at these high temperatures, and the constant pumping in of more water, which was necessary, prevented a very steady temperature being maintained. The heating was carried out in the day time and stopped at night. Every morning, before restarting, the autoclave was opened and the contents of the crucible well stirred, any loss by evaporation also being made good. Solid and solution were eventually separated and analysed. Since the filtration had to be done at the ordinary temperature, it cannot be claimed that the results obtained strictly correspond with the equilibrium solutions at the autoclave temperatures. Moreover, the amount of solution available for analysis (from 6 to 14 c.c. in different experiments) was very small considering the dilution.

The autoclave solids consisted, in the main, of very fine, crystalline material (apparently tiny prisms). In most cases some ghosts of $CaHPO_4,2H_2O$ crystals were present, and sometimes crystals (possibly pseudomorphs) of $CaHPO_4$. Solid 1 contained some perfectly fresh $CaHPO_4$ crystals.

The results obtained in the experiments at 100° and higher temperatures are given in table II. They serve at least to show that conditions at these higher temperatures are very similar to those prevailing at 25°, and they support the conclusions drawn from the more numerous results at the lower temperature.

The Graph Representing the Results at 25°.

Consideration of the curve reveals several interesting features. In the first place, it would appear that the breaks in the curve

corresponding with the transition from di- to tri-calcium phosphate and to oxyapatite are not at all marked.   From this it follows that, even at a considerable distance from the transition point, there will be relatively little difference in the stability of the stable and the unstable form.   This will help to explain the great slowness with which the changes dealt with in this paper take place.   Note in this connexion the persistence of the oxyapatite in Expt. 10 (table I).   A second very important point to note is that, of all the phosphates of calcium, oxyapatite is the only one that is not decomposed by water.   It can dissolve unchanged in pure water, although the saturated solution so obtained

Basic calcium phosphate isotherm at 25°.

CaO *per* 100 *grams of solution.*
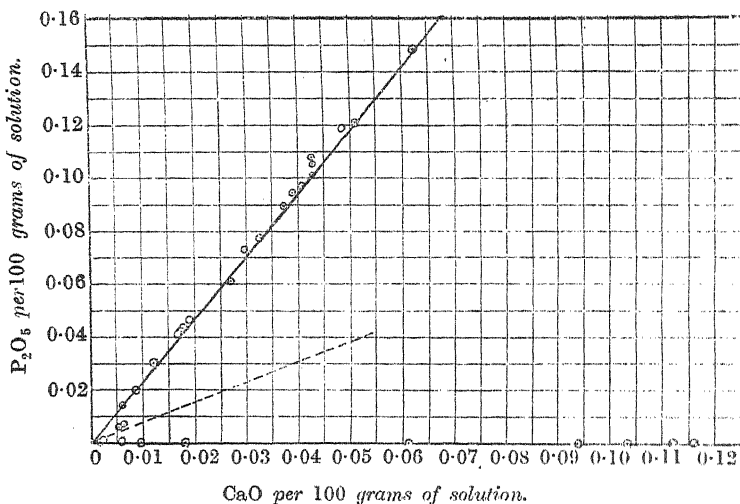
would be extremely dilute, the point on the curve corresponding with it probably falling very near to the origin of co-ordinates. The dotted line in the figure corresponds with solutions in which the ratio P_2O_5 per cent./CaO per cent. has the same value (0·761). as it has for oxyapatite itself, and, as is evident, it cuts the oxyapatite solubility curve.   If similar lines are drawn for tri-, di-, or mono-calcium phosphates, it is found that in no case do they cut the corresponding solubility curve.   Those three compounds are all decomposed by pure water.

In this connexion, it is worth referring to a paper by Warrington (*Journ. Chem. Soc.*, 1873, **26**, 983), in which it was shown that by repeatedly extracting tricalcium phosphate with boiling water,

a product was finally obtained which on analysis gave figures very near to those of hydroxyapatite. More recent work of Buch (*Zeitsch. anorg. Chem.*, 1907, **52**, 323) on the decomposition of dicalcium phosphate by water also appears to indicate that oxy- (or hydroxy-) apatite is the final product of such decomposition, although most of his experiments stopped short of that point.

Another interesting feature of the oxyapatite solubility curve is that it extends from markedly acid, through neutral, to markedly alkaline regions. Oxyapatite is the only calcium phosphate that can exist in stable equilibrium under such varied conditions. The region of acidity which it covers is of very great practical importance.

The Acid from which Hydroxyapatite is Derived.

It seems possible from the extreme slowness with which tricalcium phosphate is formed as compared with the dicalcium compound that the molecule is really a polymeride of the simple $Ca_3P_2O_8$. The compound $Ca_3P_2O_8$ is usually considered a "normal" salt, whilst oxyapatite would be called a "basic" salt. Nevertheless, there is a remarkable similarity between the two compounds, both as regards the difficulty and slowness of their formation and as regards their general properties. This would suggest that the difference between acid, normal, and basic salts is not necessarily of the kind generally assumed. The usual view seems to be that in a "basic" salt, the part of the base over and above that required to form what is considered to be the "normal" salt plays a different rôle in the molecule from that played by the rest of the base. This is brought out by the method of formulation—$(Ca_3P_2O_8)_3CaO$—which is customary, but which the author thinks is not good. He would suggest that oxy- (or hydroxy-) apatite, and possibly even tricalcium phosphate, are related to mono- and di-calcium phosphate rather in the same way that an orthophosphate is related to a pyrophosphate. Hydroxyapatite may well be a salt of an acid, $H_{11}P_3O_{13}$, in which one acidic hydrogen is still unneutralised. The remarkable difficulty with which some of the water in these preparations is expelled seems more in keeping with the view that it is directly associated with the acid rather than with the base. It would then be comparable with the "water of constitution" of certain silicate minerals which is often regarded as being directly associated with the silicic acid. The halogen in chloro- and fluoro-apatite would then have to be regarded as being directly attached to the phosphorus, and this view does not seem impossible, and is strengthened by the exist-

ence of compounds such as $CaO,2POCl_3$ (Bassett and Taylor, T.,
1911, **99**, 1402), which appears to be a chloro-derivative of mono-
calcium phosphate, $CaO,2PO(OH)_3$, usually formulated as
$CaH_4P_2O_8,H_2O$. It is perhaps worth noting that if the deficit in
the oxyapatite analyses is all due to water, it in some cases
approximates to the 3·52 per cent. required for a compound,
$(Ca_3P_2O_8)_3Ca(OH)_2,H_2O$. If all the hydrogen in such a compound
were acidic, the corresponding acid would be $H_{24}P_6O_{27} = 3(H_8P_2O_9)$.
Now $H_8P_2O_9$ is, of all the phosphoric acids, the one which has the
greatest range of existence. It is readily obtained in the crystal-
line condition, and can exist in stable equilibrium with phosphoric
acid solutions from about $-100°$ to $+27°$. It has always seemed
to the present author that more than six of these eight hydrogen
atoms should be replaceable by metals. No evidence has been
obtained in the present investigation that all of them can be
replaced by calcium—in the presence of water, that is to say—
although at first experiments seemed to indicate that; but may
it not be that the "oxyapatite" solids are really derived directly
in this way from $H_8P_2O_9$?

When considering the tenacity with which some of the water
is held in the hydroxyapatite preparations, it must, of course, be
borne in mind that this may be partly due to adsorption effects.
The preparations are probably amorphous, and amorphous com-
pounds sometimes retain water with great persistence. It is not
thought that such an explanation will suffice in the present case,
but its possibility undoubtedly complicates the problem.

The Nature of Bone Phosphate.

Blood serum and animal tissues in general have a very nearly
neutral reaction. The conditions under which bone is deposited
are, of course, more complex than those considered experimentally
during the present investigation. It is deposited from a solution
containing several metals other than calcium—more particularly
sodium, potassium, and magnesium; carbonate and chloride are
also present, so it is not surprising that all of these are found in
bone. The solubility relationships which hold for the simple
system $CaO-P_2O_5-H_2O$ will undoubtedly be modified to some extent
by the presence of additional salts, but there is reason to think
that conditions in the complex system—"bone–fluid from which
it is deposited"—will be very similar to those in the simple system.

As hydroxyapatite is the stable phase at the degree of acidity
characteristic of animal tissues, it is to be expected that it is the
essential constituent of bone phosphate. However, it is not by

any means easy to say definitely that it is.   In particular, it is
difficult to say in what form the carbonate is present.

Several papers have been published claiming the existence of
minerals ("dahllite," "podolite," etc.) of the calcium apatite group
with the halogen partly or entirely replaced by carbonic acid
(Brögger and Bäckström, *Zeitsch. Kryst. Min.*, 1890, **17**, 426;
from *Ofv. Vet. Akad. förh.*, 1888, 493; Schwantke, *Centr. Min.*,
1905, 641; Tschirwinsky, *ibid.*, 1907, 279; Schaller, *Amer. J. Sci.*,
1910, [iv], **30**, 309; Rogers, *ibid.*, 1912, [iv], **33**, 475).   Whilst
the evidence brought forward in these papers is perhaps not quite
as satisfactory as could be wished, it does seem to indicate the
possible existence of such carbonate-apatites.

Several papers deal with the question of bone carbonate.
Gabriel (*loc. cit.*), Alby (*J. pr. Chem.*, 1872, [ii], **5**, 308, also *Ber.*,
1874, **7**, 555), and Gassmann (*Zeitsch. physiol. Chem.*, 1910, **70**,
161) have suggested that the carbonate present in bone is com-
bined with the phosphate, but so far no very satisfactory con-
clusions have been reached on this point.   A number of Gabriel's
analyses of bone phosphate prepared by his method (digestion of
dry powdered bone with a glycerol solution of potassium hydroxide
at 180—200°) are given in the following table:

	Human bone.	Goose bone.	Ox bone.	Ox teeth *A*.	Ox teeth *B*.	
Per cent. of					Enamel.	Rest of teeth.
CaO	51·31	51·01	51·28	50·70	51·98	50·36
MgO	0·77	1·27	1·05	1·52	0·53	1·83
K_2O	0·32	0·19	0·18	0·20	0·20	0·14
Na_2O	1·04	1·11	1·09	1·16	1·10	0·80
Water of crystallisation	2·46	3·05	2·33	2·21	1·80	2·90
P_2O_5	36·65	38·19	37·46	38·88	39·70	38·60
CO_2	5·86	4·11	5·06	4·09	3·23	3·97
Cl	0·01	0·06	0·04	0·05	0·21	0·03
Water of constitu-tion*	1·32	1·07	1·37	1·27	1·17	1·25
Total	99·74	100·06	99·86	100·14	99·92	99·88

* This was obtained by strong ignition with silica.

Gabriel states that the potash present has not been derived from
the potassium hydroxide used in the preparation, and that the
composition of ordinary ignited bone ash is practically identical
with that of the "glycerol ash" if calculated to the same carbon
dioxide and water content.   The glycerol method undoubtedly
gives a very good product.   It is a white powder showing the
structure of the original bone and almost entirely free from organic
matter.   Gabriel noticed that on heating the "glycerol ash" over
a small flame in a platinum crucible, carbon dioxide began to be
evolved even when the bottom of the crucible was not red hot.

This led him to suppose that the carbon dioxide was present, not as calcium carbonate or magnesium carbonate, but as a phosphate-carbonate.

In the table on p. 639 are set out some figures derived from Gabriel's analyses which seem helpful in arriving at a decision as to the probable nature of bone phosphate. The "total equivalent CaO" is the actual amount of lime plus that equivalent to the small amounts of soda, potash, and magnesia also present:

The several P_2O_5/CaO ratios in the above table have been calculated (*a*) from the percentage of actual lime in the several samples; (*b*) from the total equivalent lime; (*c*) from the total equivalent lime after deducting lime equivalent to all the carbon dioxide as calcium carbonate; (*d*) from the total equivalent lime after deducting lime equivalent to all the carbon dioxide in the form of bicarbonate; and (*e*) from the total equivalent lime on the assumption that all magnesia, soda, and potash are present as bicarbonate and the rest of the carbon dioxide as calcium carbonate.

The traces of chlorine present have been ignored in making the calculations. They are so small in amount that they would make no appreciable difference to the results.

After considering all the available evidence, it seems to the present author that the following is the most reasonable assumption to make as to the nature of bone phosphate: "The mineral constituents of bone consist in the main of hydroxyapatite, $(Ca_3P_2O_8)_3Ca(OH)_2$, mixed with a certain amount of calcium carbonate. In addition to these chief constituents, there are also small amounts of the bicarbonates of magnesium, sodium, and potassium, which appear to be merely adsorbed by the phosphate, carbonate aggregate. The small amount of chloride also present is probably also adsorbed in the form of sodium chloride, although it may be present as chloroapatite."

The work described in the present paper seems to show that hydroxyapatite is the only calcium phosphate which could possibly be stable under the conditions of bone formation, whilst the conditions also make it practically certain that calcium carbonate could be deposited simultaneously with the hydroxyapatite. The finely divided, possibly amorphous, character of the phosphate, carbonate aggregate makes it certain that it will adsorb, not only water, but also some soluble salts from the fluids which bathe it, and it seems probable that the presence of small amounts of magnesia, soda, and potash is best accounted for in this way. The traces of chloride present would probably also be held by adsorption. Other possibilities than the one just mentioned are rendered

	Human bone.	Goose bone.	Ox bone.	Ox teeth A.	Ox teeth B.	
					Enamel.	Rest of teeth.
P_2O_5	36·65	38·19	37·46	38·88	39·70	38·60
Actual CaO	51·31	51·01	51·28	50·70	51·98	50·36
Total equivalent CaO	53·51	53·89	53·85	53·98	53·83	53·70
CO_2	5·86	4·11	5·06	4·09	3·23	3·97
CaO equiv. to CO_2 as $CaCO_3$	7·46	5·23	6·44	5·21	4·11	5·05
(a) $\dfrac{P_2O_5}{\text{actual CaO}}$	0·713	0·749	0·731	0·765	0·764	0·766
(b) $\dfrac{P_2O_5}{\text{total equivalent CaO}}$	0·685	0·709	0·696	0·723	0·738	0·719
(c) $\dfrac{P_2O_5}{\text{total equiv. CaO—CaO equiv. to } CO_2 \text{ as } CaCO_3}$	0·796	0·785	0·790	0·797	0·798	0·793
(d) $\dfrac{P_2O_5}{\text{total equiv. CaO—CaO equiv. to all } CO_2 \text{ as bicarbonate}}$	0·736	0·745	0·740	0·757	0·767	0·754
(e) $\dfrac{P_2O_5}{\text{total equiv. CaO—CaO equiv. to } CO_2 \text{ when } Na_2O, K_2O, \text{ and } MgO \text{ are bicarbonate and rest of } CO_2 \text{ is } CaCO_3}$	0·777	0·762	0·771	0·771	0·784	0·767

unlikely by the values of the several P_2O_5/CaO ratios tabulated above.

(*a*) These ratios would correspond with the case of all the soda, potash, and magnesia being present as carbonate or bicarbonate, and any remaining carbon dioxide being combined with the calcium phosphate. In the case of ox teeth *A* and *B*, the ratios so obtained are reasonable, but the other values are so basic as to suggest the presence of some calcium carbonate as such. As, on general grounds also, it is difficult to think that calcium carbonate is not formed in all cases, the assumption that a carbonate-apatite is formed seems unsatisfactory.

(*b*) These ratios correspond with the replacement of a certain amount of lime by soda, potash, and magnesia in a complex phosphate, which also contains all the carbon dioxide in combination. A phosphate corresponding with such highly basic values is most improbable in view of the results of the experiments quoted in this paper.

(*c*) These values, obtained on the assumption that all the carbon dioxide is present as normal carbonate (Na_2CO_3, K_2CO_3, $MgCO_3$, and $CaCO_3$), are too acid, whereas

(*d*) The figures obtained if it is assumed that only bicarbonates are present are too basic, and, moreover, the presence of any calcium bicarbonate is unlikely.

(*e*) These ratios correspond with the case which, as already indicated, seems most reasonable. The figures are as near the value 0·761 for hydroxyapatite as can be expected.

The ease with which some at least of the carbon dioxide present in bone phosphate is expelled by gentle heat is in good agreement with the view that bicarbonates of sodium, potassium, and magnesium are present, whilst the suggestion that these compounds are merely adsorbed by the phosphate, carbon aggregate is strengthened by the following experiments.

Some bone phosphate was prepared by Gabriel's method from ox bone (pelvis), from which fat was first removed by shaking with ether. Two separate quantities of the bone phosphate were shaken with distilled water in cerasin wax bottles in the thermostat at 25°. The solutions were separated and analysed after sixteen and nineteen months respectively. In each case the solution was neutral to litmus paper, but on evaporation in a platinum basin gave a strongly alkaline residue which consisted of carbonates of calcium, magnesium, sodium, and potassium, with only a mere trace of phosphate. Details are as follows:

Expt. I.—Two grams of bone phosphate and 100 c.c. of distilled

water were shaken at 25° for sixteen months.   At the end of this time the solution was found to contain:

CaO $= 0\cdot00326$ per cent.

MgO $= 0\cdot00288$,,

and $(Na_2O + K_2O)$ equivalent to CaO $= 0\cdot00176$ per cent.

The two alkalis were not determined separately, but there seemed to be a good deal more soda than potash present; $0\cdot0005$ per cent. of phosphoric oxide was also found, but this determina tion is not very trustworthy, and possibly no more phosphoric oxide was actually present than was found in Expt. II.

Expt. II.—Six grams of bone phosphate and 85 c.c. of distilled water were shaken at 25° for nineteen months.   The solution was then found to contain:

CaO $= 0\cdot00286$ per cent.

MgO $= 0\cdot00675$,,

$Na_2O = 0\cdot00743$,,

K_2O $= 0\text{-}00703$,,

$P_2O_5 = 0\cdot00005$,,

Were the bone phosphate a single compound or even a simple mechanical mixture of compounds, the composition of the equilibrium solution (and it is probable that sixteen months was long enough for equilibrium to be attained) should not be affected so greatly by variation in the proportion of solid phase to solution. Such behaviour was to be expected, however, if the magnesia, soda, and potash were merely adsorbed by the bulk of the solid. The variation in the amount of lime present in the two solutions is much less, and is such as might easily be due to the different amounts of other salts present.

Calcium Phosphates in the Soil.

Almost all that has been said in connexion with bone phosphate can be applied nearly word for word to the case of phosphates in the soil.   The range of acidity or alkalinity in most ordinary soils comes well within the range over which hydroxyapatite is the stable calcium phosphate, and it seems certain that it is the only such phosphate that can exist permanently in the soil.   Any other phosphate added to it will be converted into hydroxyapatite with greater or less readiness according to circumstances.   It has long been recognised that monocalcium phosphate added to the soil in superphosphate very quickly ceases to be present as such, although it is generally stated to revert to tricalcium phosphate.   By adding the phosphate in the form of superphosphate, the hydroxy-

apatite is obtained in a finely divided state, which is important owing to its sparing solubility. Finely ground basic slag when added to the soil will also be converted fairly quickly into hydroxyapatite, whether it contains tetracalcium phosphate, as has been suggested, or some other compound possibly more closely related to hydroxyapatite.

It is highly probable that the earthy phosphorites and coprolites are impure mixtures of hydroxyapatite and calcium carbonate, and it is known that when extremely finely ground they give satisfactory results when used directly as fertilisers.

Under the conditions which have led to the accumulation of phosphatic deposits, a certain amount of replacement of the hydroxyl of hydroxyapatite by chlorine or fluorine has occurred, owing no doubt to the action of saline solutions. Whether this also occurs to some extent in normal soils is not easy to say.

Summary.

(1) Two, and only two, phosphates of calcium more basic than dicalcium phosphate exist which can be in stable equilibrium with an aqueous solution at $25°$ (and probably at any temperature).

(2) These are tricalcium phosphate, $Ca_3P_2O_8$, and hydroxyapatite, $(Ca_3P_2O_8)_3Ca(OH)_2$.

(3) Cameron, Seidell, and Bell (*loc. cit.*) are wrong in their assumption that only a series of solid solutions exists in this region of the system $CaO-P_2O_5-H_2O$.

(4) Hydroxyapatite is the stable solid phase over a range of acidity of great practical importance, as it can exist in contact with faintly acid, neutral, and alkaline solutions.

(5) The nature of bone phosphate is discussed. It is considered to be a mixture of hydroxyapatite and calcium carbonate with small amounts of adsorbed bicarbonates of sodium, potassium, and magnesium.

(6) It is probable that hydroxyapatite is the only calcium phosphate that can permanently exist under normal soil conditions.

LVII.—" Spark–Lengths " in Various Gases and Vapours.

By Robert Wright.

The different factors affecting the phenomenon of electric dis-
charge through a gas have formed the subject of a large number
of investigations.   The object of these investigations was generally
the determination of the inter-relationship of such factors as
length and nature of spark, voltage, and gas pressure.   They have
involved a great amount of work and have been spread over a
long period of time; still, for the most part they have been
limited to the examination of the discharge through a few well-
known gases, such as air, oxygen, nitrogen, carbon dioxide, or
hydrogen.   The rather considerable difficulty of the exact deter-
mination of voltage has prevented the extension of the investiga-
tion to a larger number of gases.   A general survey of the subject
from the physical point of view will be found in Professor Sir J. J.
Thomson's " Conduction of Electricity through Gases."

The only important attempt to extend these observations to a
wider chemical field was made a number of years ago by Natterer
(*Ann. Phys. Chem.*, 1889, [iii], **38**, 663), who examined the spark
discharge through a number of gases and vapours at atmospheric
pressure, using as a source of current a small induction coil
actuated by a battery of dichromate cells.   The measurements,
which were carried out in order to determine the length of spark
obtainable in different gases and vapours for a given potential of
spark discharge, are open to two serious objections.   In the first
place, the spark used in all cases was the longest which the coil
would give, and the only attempt made to render the potential
constant was the frequent renewal of the exciting liquid of the
driving cells; it is obvious that under such conditions the voltage
must have varied to a considerable extent.   Further, the various
substances were examined at very different temperatures; gases
were used at ordinary temperature, whilst vapours were
examined at temperatures varying between 80° and 271°.   More-
over, the spark gaps used were not all of the same form, some being
made of simple platinum wires, whilst others were of the more
usual type with spherical ends.

The effect of temperature on the spark has been worked out by
Harris (*Phil. Trans.*, 1834, **124**, 230) and Cardani (*Rend. Accad.
Lincei*, 1888, **6**, 44), both workers arriving at the same result.
They found that temperature had no effect on the spark provided

that the number of molecules per c.c. of the given gas remained
constant. That is to say, if the spark gap be enclosed in a gas-
tight vessel, then the voltage required to produce a spark will be
quite independent of the temperature. If, however, the vessel be
left open, so that the gas can expand at atmospheric pressure, then
increase of temperature causes increases of spark length for a
given voltage. The effect is exactly the same as if the gas con-
centration had been reduced by lowering the pressure in the
ordinary way, the temperature remaining constant. In the present
work a 20 mm. gap at 100° was found to correspond with 15 mm.
at 18°, and 20 mm. at 183° with 5 mm. at 18°.

In the present investigation the vapours of a number of simple
organic substances have been sparked, the following precautions
being observed : (a) The form of gap used was the same in each
case, consisting of two brass spheres 5 mm. in diameter mounted on
rods of 3 mm. diameter. (b) The temperature was kept the same
throughout any series of comparisons. (c) A fairly constant
voltage was arranged for by having an air gap of similar form
and definite length coupled in parallel with the vapour gap, both
gaps being at the same temperature. In a measurement the length
of the vapour gap was adjusted, so that on carefully raising the
potential it sparked equally with the standard air gap. Thus
the measurements may be taken as representing the insulating
powers of the various substances relative to that of air at the
same temperature and pressure.

During the first part of the investigation several measurements
were made by comparing vapours at their boiling points with air
at the same temperature. This method was abandoned for
several reasons. In the first place, the heating of the standard
air gap in the vapour of the boiling liquid necessitated the
use of the latter in a quantity sufficient to provide a vapour-
bath for the standard gap, a procedure which was rather expensive
in the case of several of the substances used. Secondly, it was
found to be impossible to keep the electrodes of the vapour gap
free from condensed liquid, so that the spark took place not only
through the vapour, but also through two layers of liquid of un-
known thicknesses. This condensation effect was worst when the
gap was arranged vertically, the upper electrode being then
covered with a heavy hanging drop, but it was also present when
a horizontal gap was employed. Finally, since temperature has
a considerable effect on the voltage required to pass a spark
across the standard gap, it is evident, by using liquids of different
boiling points, a considerable variation of potential is introduced
into the series of measurements.

Although it would have been somewhat more convenient to have kept the air gap at the ordinary temperature throughout the whole of the measurements, while the vapours of any given series were heated to a second definite temperature higher than the boiling point of the least volatile member, and although by such an arrangement the same potential would—within the limits of accuracy of the method—be applied to each vapour, still it was thought advisable to heat the air gap to the same temperature as the vapour, as by so doing we are dealing with the same number of gas molecules per unit volume in each case, and so obtain better conditions for comparative measurements. Whether the air gap is heated or not, it is of the first importance that all vapours with which comparative measurements are being made should be at the same temperature.

The standard gap was mounted in a vertical glass tube of 15 mm. internal diameter surrounded by a vapour jacket. The lower electrode passes into a cork at the end of the tube, and is kept centred by being threaded through two cork disks which fit easily inside the tube, the disks being notched to admit the free passage of air. The upper end of the tube is left open and is ground flat; the upper electrode is also fitted with cork disks, and is held in position by means of a sliding stop which can be clamped on to the electrode, and acts against the ground-off end of the tube. In order to fix the air gap at a definite length, the upper electrode is removed and a small brass cylinder of the desired length (2 or 3 cm.) is lowered by means of a thread on to the top of the lower electrode; the upper electrode is then replaced so that it rests on the top of the cylinder when the stop is adjusted against the ground end of the tube and clamped to the electrode. The electrode is once more removed, the cylinder withdrawn, and the electrode reinserted. This method of adjustment was found much more convenient than working with a cathetometer, as it allows ready and accurate change of gap being made during the measurements; moreover, there is considerable difficulty in using a cathetometer with a vapour-jacketed tube, as the latter is generally covered with drops of condensed liquid which render accurate measurement impossible. The lower end of the tube surrounding the gap was fitted with a side-piece through which filtered air could be driven by means of a foot bellows, the object being the sweeping out of ionised air produced by the passage of the spark.

The tube used for the sparking of gases was the same as the air gap, except that the upper end was closed with a cork and fitted with a side-tube, the gas being led in from above or

below according as its density was less or greater than that of air.

The arrangement used for the vapour gap resembled a Victor Meyer vapour density apparatus, as can be seen from the figure.
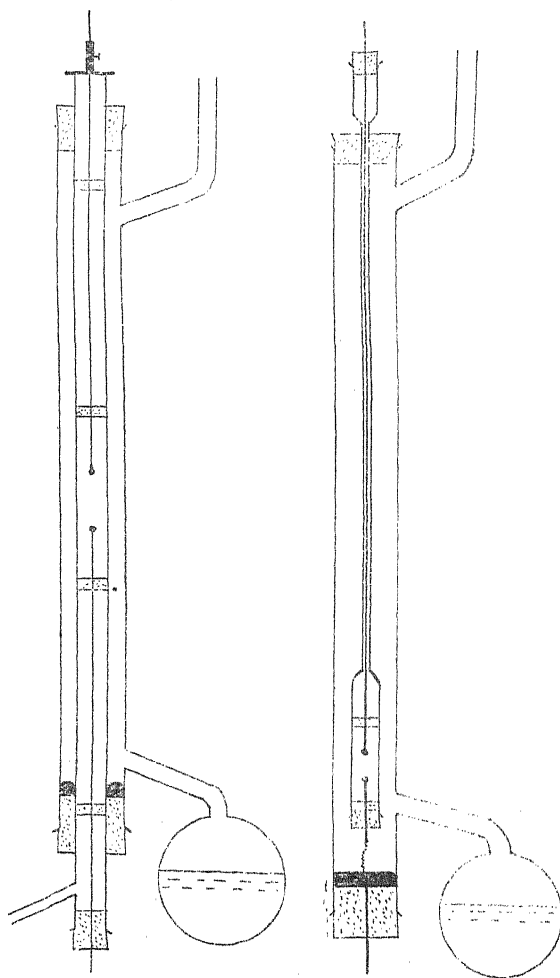
Standard air-gap.   Vapour gap.

The vapour heating jacket was closed at the lower end by a rubber stopper, through which passed a copper wire, the stopper being covered with a layer of mercury which served not only to protect the rubber from the action of boiling vapour, but also to form

electric contact with the outside of the jacket by means of the
wire through the stopper. The sparking chamber consisted of a
glass tube of 15 mm. diameter and 10 cm. long. It was closed at
its lower end by means of a wood stopper and its upper end was
joined to a tube 30 cm. long and of 4 mm. bore, this tube being
in turn joined to a short length of somewhat wider tubing. The
lower electrode passed through the cork in the bottom of the
vessel and made contact with the mercury layer in the vapour
jacket; the upper electrode, centred in the usual manner by means
of a cork disk, passed through the narrow tube, which it almost
filled, and was held in position at the upper end by means of a
cork which was slotted down the side to admit of the escape of
vapour. The entire arrangement was held in the vapour jacket
by means of a split cork. The form of sparking vessel just
described was found more suitable than one of more rigid pattern
with sealed in electrodes; for it is very necessary to be able to
take the apparatus to pieces to admit of proper cleaning, as many
of the substances examined decompose under the action of the
spark, and, moreover, the electrodes require to be polished at
frequent intervals.

In carrying out a determination, the standard air gap and the
vapour gap, together with a second adjustable air gap, are
arranged in parallel, and all three are connected with an induc-
tion coil. The third gap serves the purpose of varying the poten-
tial; it is almost closed at the beginning of an experiment, so
that, on switching on the coil, sparks only pass across the variable
gap, and as the electrodes of this gap are moved apart, the poten-
tial rises until at length a spark passes across one of the other
gaps.

The liquid in the two vapour jackets having been heated to
boiling, a small quantity of the substance under examination is
placed in the sparking vessel, which is then fixed in position in
its vapour jacket, care being taken that the lower electrode makes
contact with the mercury layer at the bottom of the jacket, and
through it with the induction coil. The liquid in the sparking
vessel at once begins to boil, and by so doing drives the air out
of the vessel; in a short time the liquid will have disappeared,
leaving the vessel full of dry vapour at the temperature of the
heating jacket. The coil is now switched on, and the electrodes
of the adjustable gap—which should be sparking strongly—
gradually drawn apart until a spark crosses one of the other gaps.
If the standard gap sparks first, fresh air is blown across it by
means of a foot bellows, and the vapour gap reduced slightly in
size, when the process is repeated, until at length both the

standard and vapour gaps spark simultaneously. It is advisable to begin the measurement with the vapour gap wide open and gradually to reduce its size until it just balances with the air gap, the reason being that many of the vapours decompose with the passage of the first spark, thus necessitating the removal and cleaning of the sparking vessel before the measurement can be proceeded with. When the two gaps balance, the vapour vessel is removed from its jacket and the distance between the electrodes measured, either using a cathetometer or more simply by winding two straight-edged paper slips round the sparking vessel so that they form bands, which are then held in position by rubber rings; the paper bands are then slipped along the glass tube of the sparking vessel until their straight edges lie in the same planes as the ends of the electrodes, when it is obvious that the distance between the bands is the same as that separating the electrodes. After measuring this distance, the sparking vessel is cleaned out and a fresh determination proceeded with.

Table of Relative Spark Lengths in mm.

Substance.	Air gap 30 mm.	Air gap 20 mm.	Temperature.
Methane	29	20	100°
Methyl chloride	24	16	100
Methylene chloride	9	6	100
Chloroform	5	3·5	100
Carbon tetrachloride	1·5	1	100
Methyl bromide	12	9	100
Methyl iodide	8·5	5·5	100
Ethane	24	18	100
Ethyl chloride	21	16	100
Ethyl bromide	9	6·5	100
Ethyl iodide	6·5	4·5	100
Ethylene	35	27	100
Acetylene	32	26	100
Water	40	36	138
Methyl alcohol	30	26	138
Ethyl alcohol	23	19	138
isoPropyl alcohol	18	15	138
isoButyl alcohol	16	13	138
Ethyl formate	14	—	138
Ethyl acetate	11	—	138
Ethyl propionate	8	—	138
Carbon dioxide	16	11	100
Sulphur dioxide	10	6	100
Carbon disulphide	8	5	100
Hydrogen sulphide	17	12	100

No claim for great accuracy of the results is put forward. Each figure tabulated is the mean of several readings, which never varied among each other by less than 10 per cent., and sometimes by a greater amount. Still, it is obvious that for any series of comparable substances, increase of molecular weight is accompanied by increase of insulating power, but the method is not sufficiently accurate to determine whether the property is a purely additive one or not. It should be noted that the spark-lengths corresponding with the 20 mm. air gap are seldom exactly two-thirds of the values obtained with the 30 mm. standard, and in some cases vary greatly from that amount. In other words, the curves connecting potential and length of spark for different gases may intersect one another. This result was actually obtained in the case of carbon dioxide and air (both gases being at the ordinary temperature), as will be seen from the following figures, which give the spark lengths in centimetres:

Air	1	2	3	4	5	6	7	8
Carbon dioxide	0·5	1	1·6 4·8	5·5	6·5	7·5	8·5	9·5

It will be seen that at low potentials carbon dioxide is a better insulator than air, whilst at higher potentials the reverse is the case.

The purification of the substances scarcely requires mention, as they are all well-known compounds. Methane and ethane were prepared from the respective alkyl iodides, whilst the other substances were obtained and purified by the ordinary methods.

An attempt was also made to measure the spark-length for several of the substances in the liquid state. For this purpose, the upper electrode was mounted on a micrometer screw, so that the spark-length might be measured accurately. The results, however, did not prove satisfactory; several of the liquids formed electrolytic conductors, possibly on account of impurities derived from the electrodes, whilst the few that were measured did not yield concordant results. It is scarcely to be expected, however, that any simple agreement could exist in the case of liquids, for not only has the extra factor of surface tension been introduced, but, in addition, the simple relationship between the number of molecules and the volume which holds for gases no longer exists.

LVIII.—*Constitution of the Salts of s-Alkylthio-carbamides.*

By JOHN TAYLOR.

COMPOUNDS of thiocarbamide with alkyl haloids were first described by Claus (*Ber.*, 1874, **7**, 236; 1875, **8**, 41; *Annalen*, 1875, **179**, 145). The work was reviewed and extended by Bernthsen and Klinger (*Ber.*, 1878, **11**, 492; 1879, **12**, 575), who showed that the alkyl group was linked to the sulphur atom of thiocarbamide, formulating the substance thus, $NH_2 \cdot C(:NH) \cdot S \cdot R, HX$; the compound with benzyl chloride was further examined by E. A. Werner (T., 1890, **57**, 283). Other investigators have examined the additive products of alkyl haloids with substituted thiocarbamides.

An additive compound of thiocarbamide and ethyl oxalate has been described by Nencki (*Ber.*, 1874, **7**, 780).

Werner (*loc. cit.*) transformed thiocarbamide benzyl chloride * to sulphate by the use of sulphuric acid, $CSN_2H_4, C_6H_5 \cdot CH_2Cl \xrightarrow{H_2SO_4}$ $(CSN_2H_4)_2(C_6H_5 \cdot CH_2)_2SO_4$. He also records the transformation of thiocarbamide allyl bromide to sulphate by heating its alcoholic solution with silver sulphate,

$$CSN_2H_4, C_3H_5Br \xrightarrow{Ag_2SO_4} (CSN_2H_4)_2(C_3H_5)_2SO_4.$$
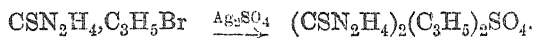
Arndt (*Annalen*, 1911, **384**, 331) prepared several salts of ψ-thioureas by combining them with various acids. He, however, was content with preparing the salts, and gave no indication of their structure:

$$NH_2 \cdot C(:NH) \cdot SR + HX \longrightarrow NH_2 \cdot C(:NH) \cdot SR, HX.$$
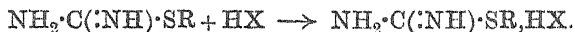
The present investigation seeks to extend the range of additive compounds, to suggest a structure indicating the position of the acidic group, and to show that compounds similar to the direct additive products may be prepared by indirect means.

It has now been found that thiocarbamide unites additively with alkyl sulphates, nitrates, and thiocyanates. These additive products were obtained by heating together, in alcoholic solution, thiocarbamide and a slight excess of the required ester.

Methyl esters combined most readily; next in order came benzyl esters, and lastly ethyl esters. This order is the same as holds in the case of combination of thiocarbamide with the alkyl haloids. It is probable that this order corresponds with the order of ease

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* This nomenclature is used instead of the more cumbrous "the chloride of benzyl-ψ-thiourea" or "the additive compound of benzyl chloride with thiocarbamide."

of hydrolysis of the esters. In the case of the thiocyanates, it certainly corresponds with the order of ease of transformation of thiocyanate to thiocarbimide. In conformity with this view, it may be added that allyl thiocyanate, the most easily transformed of all the thiocyanates, combines completely, in the cold, on long contact with thiocarbamide, whilst phenyl thiocyanate, which shows no tendency towards transforming to thiocarbimide, gave no indication of combination even when boiled with thiocarbamide.

Substances similar to the additive products may be obtained by indirect means; thus the same compound was obtained by (a) combining benzyl chloride with thiocarbamide, and (b) the action of barium chloride on thiocarbamide benzyl sulphate. Compounds with methyl thiocyanate and nitrate obtained by these methods were also identical.

Since esters of organic acids failed to combine directly with thiocarbamide, advantage was taken of the method of double decomposition to obtain them indirectly. Their general sparing solubility in water served to render their isolation quite easy. For example, thiocarbamide methyl salicylate was precipitated on mixing aqueous solutions of sodium salicylate and thiocarbamide methyl sulphate. Under no condition that was tried could methyl salicylate be made to combine directly with thiocarbamide.
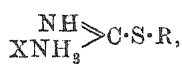
When direct addition of an ester to thiocarbamide takes place, the alkyl group becomes linked to sulphur. The acyl group may enter any one of three possible positions:

$$\frac{NH_2}{NH_2}{>}C{:}S{<}\frac{R}{X} \qquad \frac{NH_2}{NH_2}{>}\underset{X}{C{\cdot}S{\cdot}R} \qquad \frac{NH}{XNH_3}{>}C{\cdot}S{\cdot}R,$$
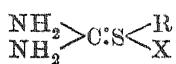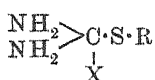
$$(a.) \qquad\qquad (b.) \qquad\qquad (c.)$$

which for convenience may be designated (a) sulphonium, (b) carbonium, and (c) ammonium compounds.

These additive products all behave like salts of a strong base. All are more or less readily soluble in water. Their solutions are neutral to litmus, give picrates on the addition of picric acid, and respond to the usual tests for the acidic ion. As a rule, organic compounds which have these acid groups directly linked to carbon are not at all freely ionised; thus ethyl potassium sulphate, ethyl oxalate, and ethyl thiocyanate do not respond to the ordinary tests for the acid radicles. This universal and strong ionisation of the additive products points to the improbability of the carbonium form (b).

Two observations point to the improbability of the ammonium form. First, thiocarbamide benzyl nitrite may be recrystallised from boiling water. Compounds which contain a nitrite group

directly linked to nitrogen are well known to be unstable. It seems unlikely that the compound $NO_2 \cdot NH_2 \cdot C(:NH) \cdot S \cdot R$ could be stable enough to be recrystallised from boiling water. Secondly, solutions of thiocarbamide methyl thiocyanate and of thiocarbamide benzyl thiocyanate, were evaporated repeatedly to dryness, and the substances fused without any noticeable change in properties. Amine thiocyanates when heated undergo transformation to thiocarbamides, $NH_3Ph \cdot SCN \longrightarrow NHPh \cdot CS \cdot NH_2$, $NH_4SCN \longrightarrow NH_2 \cdot CS \cdot NH_2$. A compound of the type $R \cdot S \cdot C(:NH) \cdot NH_2 \cdot SCN$ should yield with ease $R \cdot S \cdot C(:NH) \cdot NH \cdot CS \cdot NH_2$, which, in turn, would give hydrogen sulphide to an alkaline solution of a lead salt. The thiocyanates mentioned above gave after such treatment no trace of lead sulphide when heated with an alkaline solution of lead acetate. Hence in these products, which were obtained either by direct addition or by double decomposition, the acidic group does not form an ammonium compound.

The only remaining possibility is the sulphonium linking. Here both alkyl and acyl groups unite directly with sulphur, thus: $(NH_2)_2CS + RX \longrightarrow (NH_2)_2C:SRX$. This view of the grouping is not opposed to any of the observed facts.

Sulphonium compounds are well known, and are either well-marked bases or salts. Their properties are very similar to those of the thiocarbamide additive products. Both are crystalline and soluble in water. Their solutions are highly ionised, and hence new salts may be prepared by double decomposition, consequently there is nothing improbable in the idea that these compounds are sulphonium salts.

Werner (T., 1912, **101**, 2184) considers it probable that thiocarbamide, under the influence of strongly ionised acids, gives an ammonium compound, $XNH_3 \cdot C(:NH) \cdot S \cdot R$. In this connexion, interesting observations were made with benzyl additive compounds, and it seems possible that with these both ammonium and sulphonium forms of compounds with strong acids may exist. Two distinct thiocarbamide benzyl sulphates were obtained, one, already described by Werner (*loc. cit.*), by heating together thiocarbamide benzyl chloride and sulphuric acid, and the other by heating an alcoholic solution of thiocarbamide benzyl chloride with silver sulphate. The two forms give identical analytical figures for "sulphate," but show many differences. Werner's sulphate melts at 144—145,* is exceedingly readily soluble in alcohol, and crystallises from its alcoholic solution in stout rhombs. The compound from silver sulphate melts at 180—181°, is sparingly soluble in alcohol, and crystallises from this solution in long needles. Each

* Werner gives 132—133°.

may be transformed into the other, Werner's to the sulphate of higher melting point by boiling with a feebly alkaline substance, such as a trace of sodium phosphate, or even by recrystallising from boiling water; the substance of higher melting point to Werner's sulphate, by heating with excess of dilute sulphuric acid. Werner's sulphate was also prepared by dissolving benzyl-ψ-thiourea in excess of dilute sulphuric acid and by heating thiocarbamide sulphate, CSN_2H_4,H_2SO_4, with benzyl alcohol. In every case, therefore, free sulphuric acid was present when Werner's sulphate was prepared. It seems probable that there are two isomeric compounds differing from one another in the point of attachment of the acid group, free acid determining the ammonium form, whilst feeble alkali determines the sulphonium form, thus:
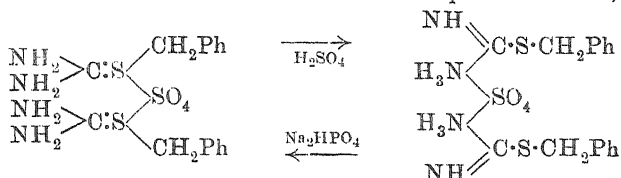
This transformation is effected by the use of "strong" acids only. Thiocarbamide benzyl acetate was recovered unchanged after recrystallisation from acetic acid. Werner also states (*loc. cit.*) that acetic acid has little or no power to change the configuration of thiocarbamide. A similar negative result was obtained with the thiocyanate and thiocyanic acid.

The electrical conductivities of equally concentrated aqueous solutions of the two forms of thiocarbamide benzyl sulphate were compared. At about 1·5 per cent. concentration, the solution of the ammonium form, which is the more readily soluble, conducted electricity 3·2 times as readily as the second solution. This great difference in conductivity points to differences in structure. Moreover, the ammonium forms melt at a lower temperature than the corresponding sulphonium forms.

There are similarly two modifications of thiocarbamide benzyl chloride, namely, a form of higher melting point produced by direct combination of the constituents in a non-ionising solvent, such as acetone, melting at 174°, and a form of lower melting point (148°) produced from the first by twice recrystallising it from hydrochloric acid, in which it is sparingly soluble. The transformation to sulphonium form is less easy than with the sulphate, but it may be accomplished by boiling the alcoholic solution with sodium phosphate—the aqueous solution is not affected by this treatment—and then keeping the resulting crystals in the steam-oven for a few hours.
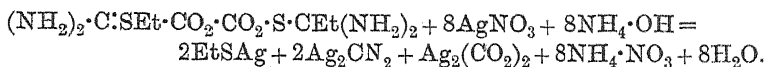
Indications of two nitrates were observed. Thus, benzyl-ψ-thiourea dissolved in nitric acid gave, first, flattened needles melting at 118°; the mother liquors from these gave a much smaller crop of nearly square plates melting at 92°. Recrystallisation from alcohol converted these to the sulphonium form melting at 118°.

No indications of two thiocyanates were observed.

The existence of sulphonium and of ammonium forms appears to be confined to the benzyl derivatives. The thiocarbamide compounds of methyl nitrate and of methyl sulphate were recovered unchanged after recrystallisation from their respective acids.

It is noteworthy that when a salt is produced by double decomposition, the product is nearly always of sulphonium form, whether the original material is sulphonium or ammonium. Thus the products of double decomposition of "sulphonium" and of "ammonium" thiocarbamide benzyl sulphate with barium nitrate were identical, melting at 118°. The same sulphate of higher melting point was prepared by the interaction of silver sulphate and either the "ammonium" or "sulphonium" forms of thiocarbamide benzyl chloride.

An interesting isomeride of Nencki's thiocarbamide ethyl oxalate was obtained by heating an alcoholic solution of thiocarbamide ethiodide with silver oxalate. Nencki's product may be regarded as a molecular compound of ethyl oxalate with thiocarbamide, whilst the new compound may be described as the oxalate of ethyl-ψ-thiourea, $(NH_2)_2C:SEt\cdot CO_2\cdot CO_2\cdot S\cdot CEt(NH_2)_2$, or an ionic compound of the above-mentioned substances. The differences between the two are quite sharp, and are such as would be expected between a molecular compound of thiocarbamide with non-ionised ethyl oxalate and a highly ionised oxalate of a sulphonium base. The former does not yield calcium oxalate until after hydrolysis with alkali hydroxide, nor does it give a picrate; the latter readily gives, in aqueous solution, both calcium oxalate and a picrate. The former yields metallic sulphide with an alkaline solution of a lead salt and with ammoniacal silver nitrate. The latter under similar treatment yields metallic mercaptide and cyanamide,

$$(NH_2)_2\cdot C:SEt\cdot CO_2\cdot CO_2\cdot S\cdot CEt(NH_2)_2 + 8AgNO_3 + 8NH_4\cdot OH =$$
$$2EtSAg + 2Ag_2CN_2 + Ag_2(CO_2)_2 + 8NH_4\cdot NO_3 + 8H_2O.$$

A sharp difference in fusibility was noted between the two substances, Nencki's melting at 158°, whilst the other melts at 188°.

This sharp difference in properties between the two oxalates serves to indicate the course of the reaction between salts of thiocarbamide and other compounds. It was suggested by Dixon and Taylor (T., 1916, **109**, 1245) that when thiocarbamide hydro-

chloride reacted with acetaldehyde, it was probable that the acid first migrated from thiocarbamide to acetaldehyde, and that the acid compound of the acetaldehyde in turn united with free thiocarbamide, but no direct proof could be given.

It is now found that when the thiocarbamide oxalate is heated with ethyl alcohol, Nencki's compound results.   Clearly ethyl oxalate is first formed and this afterwards unites with thiocarbamide. Therefore the acid migrates from thiocarbamide to alcohol in this case, and presumably to acetaldehyde in the preceding case.

A somewhat similar indication was observed with thiocarbamide nitrate.   When this compound was heated with methyl alcohol or with benzyl alcohol, reduction of the nitric acid occurred exactly as if the acid had been heated with alcohol without having been freed from nitrous acid by heating with carbamide.   It is evident that the hold of thiocarbamide for acid is very feeble.

Experimental.

Thiocarbamide and Sulphates.

Methyl Sulphate.—Thiocarbamide and methyl sulphate were heated together on a water-bath without any solvent.   After a few minutes a vigorous reaction took place, which was moderated by cooling.   The product, a brownish-orange paste, was heated with alcohol, when a white powder of microcrystalline needles was left undissolved.   This powder was readily soluble in water. The aqueous solution gave all the reactions for a sulphate.   When it was heated with sodium hydroxide, methyl mercaptan was liberated.   Alkaline solution of lead acetate gave a yellow precipitate of lead mercaptide, but no lead sulphide.   Ammoniacal solution of silver nitrate gave at first a white precipitate, which on heating turned yellow.   Silver mercaptide and silver cyanamide were formed, but no silver sulphide.

The substance was apparently the sulphate of methyl-ψ-thiourea, $(CSN_2H_4)_2Me_2SO_4$.   Analysis :

0·317 gave 0·255 $BaSO_4$. $SO_4 = 33\cdot14$.

$C_{11}H_{14}O_4N_{11}S_3$ requires $SO_4 = 33\cdot71$ per cent.

A similar product was obtained by heating thiocarbamide sulphate with methyl alcohol.   Thiocarbamide was dissolved in half its weight of sulphuric acid, and to this was added excess of methyl alcohol.   After short heating on a water-bath, a yellow, amorphous powder formed which was rejected, and the heating of the solution continued until no silver sulphide was formed on adding ammoniacal silver nitrate solution to a drop of the liquid.

On cooling, thin plates separated, which behaved in all respects like the direct additive product. Each decomposed at 235°. Each gave a bright yellow picrate (m. p. 221°) which may be recrystallised easily from hot water.

The latter method of preparing the substance affords a convenient method of producing material as starting point for obtaining other derivatives of methyl-ψ-thiourea.

Ethyl Sulphate.—This substance reacted with thiocarbamide under similar conditions and in just the same way as methyl sulphate, except that heating had to be continued for a much longer time.

The sulphate, $(CSN_2H_4)_2Et_2SO_4$, crystallises in tufts of white needles melting and decomposing at 202°. Its picrate melts at 186°. Analysis:

0·302 gave 0·226 $BaSO_4$. $SO_4 = 30\cdot86$.

$C_6H_{18}O_4N_4S_3$ requires $SO_4 = 31\cdot22$ per cent.

An exactly similar product was obtained, but only in small yield, by allowing thiocarbamide sulphate and ethyl alcohol to remain together in the cold for three or four days.

Benzyl Sulphate.—An alcoholic solution of thiocarbamide benzyl chloride was heated on a water-bath for a few hours with silver sulphate. The filtrate gave white, silky needles free from chloride which melted and decomposed at 180—181°. These were somewhat sparingly soluble in alcohol and readily so in water. The aqueous solution gave the usual tests for sulphate and for ψ-thiourea. The picrate from this substance melted at 183°, as does the picrate from thiocarbamide benzyl chloride described by Werner (*loc. cit.*).

The same sulphate was obtained when either the " ammonium " or " sulphonium " form of thiocarbamide benzyl chloride was employed as starting point:

0·249 gave 0·132 $BaSO_4$. $SO_4 = 21\cdot84$.

$C_{16}H_{22}O_4N_4S_3$ requires $SO_4 = 22\cdot32$ per cent.

The " ammonium " form was obtained when thiocarbamide sulphate was heated with benzyl alcohol on a water-bath for half an hour, and the whole allowed to remain for a day. The resulting creamy paste was filtered and the residue crystallised from alcohol. The product melted at 143—144°, and agreed in all respects with Werner's sulphate.

This same form of the sulphate was also prepared by dissolving benzyl-ψ-thiourea in excess of hot dilute sulphuric acid. On cooling the solution, crystals melting at 143° separated (see Arndt, *loc. cit.*).

The specific conductivities of solutions of " ammonium " and of

"sulphonium" thiocarbamide benzyl sulphate were measured in a cell the constant of which was 0·105.

With a solution of 2·5 grams in 200 c.c., the solution of the "ammonium" form had a resistance of 8·8 ohms, whilst the "sulphonium" form, had a resistance of 28·0 ohms. The equivalent conductivities are therefore 205·2 and 64·5 respectively.

Thiocarbamide and Nitrates.

Methyl Nitrate.—Thiocarbamide and methyl nitrate in methyl alcohol were heated on a water-bath for two or three hours. The solution gave rhombs which melted at 109—110°, and this melting point was not changed when the substance was recrystallised from nitric acid. The substance was soluble in water, and the aqueous solution responded to the usual tests for ψ-thiourea with an alkaline solution of lead acetate and with an ammoniacal solution of silver nitrate. It dissolved readily in methyl or ethyl alcohol:

0·250 gave 39·0 c.c. NO at 17° and 755 mm. N (nitratic) = 9·16.

$C_2H_7O_3N_3S$ requires N (nitratic) = 9·15 per cent.

An attempt to prepare the substance from thiocarbamide nitrate and methyl alcohol failed. With excess of methyl alcohol, no sign of combination was observed after an hour on a water-bath. On concentrating the solution to smaller bulk, a vigorous reduction of nitric acid took place; no thiocarbamide methyl nitrate could be detected.

A product similar to the direct additive product was obtained on mixing aqueous solutions of thiocarbamide methyl sulphate and barium nitrate. From the filtrate a substance was obtained melting at 108—109° and having the same crystal shape and chemical properties as the direct additive product. The two substances gave identical picrates (m. p. 221°).

Ethyl Nitrate.—Thiocarbamide and ethyl nitrate were heated together with alcohol on a water-bath at intervals for nearly a month. Considerable interaction had taken place, as the resulting solution gave only a slight blackening when heated with alkaline lead acetate solution. A picrate was obtained (m. p. 186°) similar to all the picrates obtained from ethyl-ψ-thiourea compounds.

Attempts to prepare the substance by the interaction of ethyl alcohol and thiocarbamide nitrate failed, just as in the case of methyl nitrate.

The action of silver nitrate on thiocarbamide ethiodide resulted in the formation of double silver salts.

Benzyl Nitrate.—This compound was prepared by mixing hot

concentrated solutions of either thiocarbamide benzyl chloride or benzyl sulphate and potassium nitrate. White, flattened needles separated from the cooled liquid, which when recrystallised from water melted at 118—119°.

The substance prepared by Arndt's method of dissolving benzyl-ψ-thiourea in nitric acid agreed in all respects with the material as prepared above. The melting point of a mixture of the two remained unchanged, showing their identity.

Analysis was carried out by adding an ammoniacal solution of silver nitrate to a weighed quantity of material in aqueous solution. The compound was completely decomposed according to the equation:

$$(NH_2)_2C\colon S(CH_2Ph)\cdot NO_3 + 3AgNO_3 + 4NH_4\cdot OH =$$
$$CN_2Ag_2 + CH_2Ph\cdot 8Ag + 4NH_4\cdot NO_3 + 4H_2O.$$
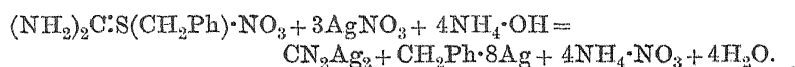
The filtered precipitate of silver cyanamide and silver benzyl mercaptide was treated with nitric acid, and the amount of silver in solution determined by Volhard's method. One hundred parts of the substance gave 139·6 parts of silver, whereas 100 parts of $CSN_2H_4,CH_2Ph\cdot NO_3$ require 141·5 parts of silver.

The nitrate readily separates on cooling a mixture of nitric acid with a hot concentrated solution of thiocarbamide benzyl chloride (compare Arndt, *loc. cit.*).

Attempts to prepare thiocarbamide benzyl nitrate from a mixture of thiocarbamide nitrate and benzyl alcohol failed in the same way as with methyl alcohol and with ethyl alcohol.

Identical products (m. p. 117—118°) were obtained by the addition of barium nitrate to solutions of either "sulphonium" or "ammonium" thiocarbamide benzyl sulphate.

Thiocarbamide and Benzyl Chloride.

Werner's work on thiocarbamide benzyl chloride (*loc. cit.*) was revised in the light of the previous experiments. He stated that on three occasions he obtained specimens which melted at 142—143°. On other occasions his product melted at 174°. He suggested the existence of polymeric modifications. It is now found that when a non-hydrolysing solvent, such as acetone, is used, no substance of lower melting point is formed. Repeated recrystallisation of the product from hydrochloric acid, in which it is much less readily soluble than in water, yielded thin, glistening plates which melted at 148°. This appears to be the "ammonium" form of the compound. The melting point of this form, following the general rule, is lower than that of the corresponding "sulphonium" form.

After the "ammonium" form has been heated in alcoholic solution for about an hour with animal charcoal and sodium phosphate, the material becomes less readily soluble in alcohol, and the crystals show scarcely any softening at the lower temperature, and if they are further heated in a steam-oven for two or three hours the substance melts at 174° without previous softening. A mixture of the two forms is, however, very readily obtained, recrystallisation from water being sufficient to transform part from "sulphonium" form to "ammonium" form. A mixture of the two forms was produced when either the "sulphonium" or "ammonium" form of thiocarbamide benzyl sulphate was transformed to chloride by barium chloride.

The hydrochloride of benzyl-ψ-thiourea may be prepared easily by dissolving the ψ-thiourea in an excess of hot dilute hydrochloric acid. The crystals which separate on cooling melt at 148° and are identical with the "ammonium" form of thiocarbamide benzyl chloride (compare Arndt, *loc. cit.*).

An exactly similar product, melting at 148°, was prepared by heating thiocarbamide hydrochloride with benzyl alcohol.

Thiocarbamide and Thiocyanates.

These compounds are the more interesting, as all attempts to combine thiocarbamide with thiocyanic acid have failed up to the present (Krall, T., 1913, **103**, 1383).

The compounds now obtained are ionic, giving the usual reactions for thiocyanates, unlike the parent materials.

Methyl Thiocyanate.—Thiocarbamide methyl thiocyanate and alcohol were heated together on a water-bath for two or three days. A considerable quantity of solid separated which melted and decomposed at 78—80°, and was very readily soluble in water or alcohol. The usual ψ-thiocarbamide reactions were shown, as well as those for thiocyanate. It yielded a picrate melting at 220°:

0·242 required 16·1 c.c. $N/10$-$CuSO_4$.   SCN = 38·6.

$C_3H_7N_3S_2$ requires SCN = 38·9 per cent.

This compound gave no sulphide when heated with an alkaline solution of lead acetate or with an ammoniacal solution of silver nitrate, nor was sulphide produced by this treatment after solutions of the substance had been repeatedly evaporated on a water-bath and the substance itself maintained in a state of fusion for several hours.

An exactly similar product melting at 78—79° was prepared by the interaction of solutions of thiocarbamide methyl sulphate and of barium thiocyanate.

Ethyl Thiocyanate.—Complete combination of the thiocarb-amide could not be effected. Interaction took place, as the solution gave a picrate and lead mercaptide. Ammoniacal silver gave silver sulphide, indicating unchanged thiocarbamide. The product was a faintly brown paste.

Benzyl Thiocyanate.—Thiocarbamide was heated on a water-bath with benzyl thiocyanate and alcohol. After five or six hours reaction was complete. The product separated in bundles of long, slender needles which melted at 82—84°, and this melting point was unchanged by recrystallisation from thiocyanic acid, but its crystal shape became transformed to thin, hexagonal plates.

Found: $SCN = 25.58$.

$C_9H_{11}N_3S_2$ requires $SCN = 25.78$ per cent.

A product crystallising in long needles, but melting at 85—86°, was prepared by dissolving benzyl-ψ-thiourea in thiocyanic acid. On recrystallisation from thiocyanic acid, hexagonal plates melting at 82—84° were again obtained. None of these products gave hydrogen sulphide to alkaline lead acetate after heating to the fusion point. When heated more strongly, the substance dissociated, giving benzyl thiocyanate, and the fusion now readily gave metallic sulphides.

Allyl Thiocyanate.—To an alcoholic solution of allyl thiocyanate was added finely divided thiocarbamide, and this mixture allowed to remain, with occasional shaking, for nearly a month until the liquid gave none of the reactions for thiocarbamide. The product was a clear, yellow oil. One hundred parts of the substance gave 184.3 parts of silver, whereas 100 parts of $CSN_2H_4,C_3H_5\cdot SCN$ require 185.1 parts of silver.

Thiocarbamide and Benzyl Nitrite.

From an aqueous solution of thiocarbamide benzyl chloride and sodium nitrite this compound separated in fine needles. Its melting point (126°) was determined by plunging the melting-point tube into an already heated bath. Identical products were obtained with either "ammonium" or "sulphonium" thiocarbamide benzyl chloride as starting point. Nitrous acid was liberated by dilute acids, and the substance responded to the usual tests for ψ-thiocarbamide. One hundred parts of the substance gave 143 parts of silver, whereas 100 parts of $CSN_2H_4,C_6H_5\cdot CH_2\cdot NO_2$ require 145.2 parts of silver.

Arndt prepared a similar substance from benzyl-ψ-thiourea in an acid solution. He gave the same melting point for his product, but did not check its composition.
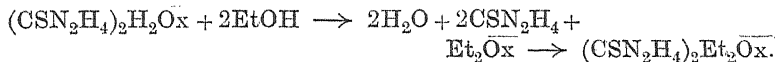
Thiocarbamide and Oxalates.

Ethyl Oxalate.—Nencki (*Ber.*, 1874, **7**, 780) and Claus (*Ber.*, 1875, **8**, 43) prepared an additive compound of thiocarbamide with ethyl oxalate, which melts at 158° and does not respond to any of the tests for ψ-thiourea or for oxalate.

An isomeride, $(CSN_2H_4)_2(CO_2Et)_2$, has now been obtained by the interaction of silver oxalate and thiocarbamide ethiodide. To the ethiodide, dissolved in alcohol, was added finely powdered silver oxalate. A considerable rise of temperature occurred and silver iodide was formed. After heating for about ten minutes on a water-bath, the hot mixture was filtered. A white, crystalline deposit of small rhombs melting at 187—189° was formed which contained no silver or halogen. It was readily soluble in water, and the solution at once responded to the tests for oxalate and for ψ-thiourea:

0·331 gave CaOx equivalent to 22·4 c.c. $N/10$-KMnO$_4$, corresponding with "oxalate" = 29·7.

$C_8H_{18}O_4N_4S_2$ requires "oxalate" = 29·8 per cent.

Attempts to prepare this substance by heating thiocarbamide oxalate with ethyl alcohol resulted in the formation of Nencki's compound, melting at 155°. The course of the reaction may be represented thus:

$$(CSN_2H_4)_2H_2Ox + 2EtOH \longrightarrow 2H_2O + 2CSN_2H_4 +$$
$$Et_2\overline{Ox} \longrightarrow (CSN_2H_4)_2Et_2\overline{Ox}.$$

Benzyl Oxalate.—This compound was obtained in thin, long, oblong plates melting at 191—192° on recrystallising from hot water the precipitate formed on mixing aqueous solutions of thiocarbamide benzyl chloride and ammonium oxalate. Its chemical behaviour is similar to that of the preceding compound:

0·313 gave CaOx equivalent to 14·8 c.c. $N/10$-KMnO$_4$, corresponding with "oxalate" = 20·81.

$C_{18}H_{22}O_4N_4S_2$ requires "oxalate" = 20·85 per cent.

The same compound also resulted from the interaction of (*a*) thiocarbamide benzyl chloride and silver oxalate (m. p. 192°), and (*b*) equivalent quantities of benzyl-ψ-thiourea and oxalic acid in alcoholic solution (m. p. 188°).

Thiocarbamide and Salicylates.

Methyl Salicylate.—Methyl salicylate and thiocarbamide failed to unite at the boiling point of methyl salicylate. The ionic compound was precipitated on mixing hot concentrated solutions of

thiocarbamide methyl sulphate and sodium salicylate. The substance crystallises in long needles which decompose at 155°. Its chemical behaviour is similar to that of other salts of ψ-thioureas. One hundred parts of the substance gave 142·8 parts of silver, whereas 100 parts of $CSN_2H_4,HO·C_6H_4·CO_2Me$ require 142·2 parts of silver.

Benzyl Salicylate.—The compound was prepared from thiocarbamide benzyl chloride and sodium salicylate. It crystallises in fine needles which melt at 144—145°. One hundred parts of the substance gave 107·5 parts of silver, whereas 100 parts of $CSN_2H_4,HO·C_6H_4·CO_2·CH_2Ph$ require 104·9 parts of silver.

Thiocarbamide and Acetates.

Ethyl Acetate.—This ester does not combine directly with thiocarbamide, but when thiocarbamide ethiodide in alcoholic solution was heated with its own weight of silver acetate for three to four hours, the solution deposited, on cooling, white, short prisms of the required compound which decomposed at 151—152°. One hundred parts of the substance gave 178·3 parts of silver, whereas 100 parts of $CSN_2H_4,CH_3·CO_2Et,H_2O$ require 178·0 parts of silver.

The substance therefore contains water of crystallisation. Arndt (*loc. cit.*) prepared the acetate of benzyl-ψ-thiourea, and showed that it also contained water of crystallisation. None of the other salts examined possessed this property.

Benzyl Acetate.—The compound of this ester with thiocarbamide separated in long, flattened needles on cooling hot mixed solutions of excess of sodium acetate with thiocarbamide, the benzyl chloride, or either of the two forms of the benzyl sulphate. It melts to a brown liquid at 135—136°, and its melting point and crystal shape are unchanged by recrystallisation from acetic acid.

The compound prepared by dissolving benzyl-ψ-thiourea in acetic acid has the same melting point and the same properties as the one prepared by double decomposition (compare Arndt, *loc. cit.*). One hundred parts of the substance gave 132·7 parts of silver, whereas 100 parts of $CSN_2H_4,CH_3·CO_2·CH_2Ph,H_2O$ require 132·7 parts of silver.

Thiocarbamide and Phosphates.

Ethyl Phosphate.—The thiocarbamide compound of this ester was obtained by heating an alcoholic solution of thiocarbamide ethiodide with silver phosphate. The product is sparingly soluble in alcohol and readily so in water. It crystallises from alcohol in

shining leaves which decompose at 195—196°. Its composition was checked by the silver method. Owing to the exceeding solubility of silver phosphate in ammonia, this was recovered by careful neutralisation of the ammoniacal liquors after the first precipitation. One hundred parts of the substance gave 303·3 parts of silver, whereas 100 parts of $(CSN_2H_4)_3(C_2H_5)_3PO_4$ require 305·3 parts of silver.

Benzyl Phosphate.—The product was obtained by mixing equal weights of thiocarbamide benzyl chloride and sodium ammonium phosphate in hot aqueous solution. An oil formed which presently hardened to crystals. The substance is sparingly soluble in alcohol, and when crystallised from hot water it forms small, fine needles decomposing at 191°. One hundred parts of the substance gave 216 parts of silver, whereas 100 parts of $(CSN_2H_4)_3(CH_2Ph)_3PO_4$ require 217·4 parts of silver.

An exactly similar product decomposing at 191° was obtained on mixing alcoholic solutions of benzyl-ψ-thiourea and phosphoric acid.

My thanks are due to Prof. A. E. Dixon for kindly criticism and interest shown during the course of this investigation, and to Mr. P. Belas for measuring the conductivity of the solutions.

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LIX.—*Phosphorescent Zinc Sulphide.*

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THE study of the conditions producing phosphorescence has given rise to an extensive literature,[*] but it cannot be said that much clear light has been thrown on the problem. Data given by one observer are contradicted by other workers, and it appears in general that the various investigators did not take sufficient care to define the conditions under which they worked, so that attempted repetitions of the work were hindered by a lack of exact knowledge of the experimental conditions employed by earlier investigators. The present work was carried out with a view to define more clearly the various factors which are concerned in the production of phosphorescent zinc sulphide.

* See Kayser, "Handbuch der Spektroscopie," Vol. IV.

In order to make clear what is unavoidably a somewhat com-
plex subject, it will be best to deal separately with the following
eight questions which arose in the course of the investigations :

I. The phosphorescence of pure zinc sulphide.

II. The influence of traces of impurities on phosphorescence.

III. The means by which impurities can be introduced.

IV. The influence exerted by the conditions under which the
zinc sulphide is precipitated.

V. The treatment of the zinc sulphide precipitate before
drying.

VI. The influence of temperature on the production of phos-
phorescent zinc sulphide.

VII. The methods of testing the final product.

VIII. The influence of appreciable quantities of impurities on
the phosphorescence.

I. *The Phosphorescence of Pure Zinc Sulphide.*—The data
respecting the power of phosphorescence possessed by pure zinc
sulphide are often contradictory. Some authors state that the
presence of a trace of impurity is necessary in order to obtain
phosphorescent specimens, whilst other investigators find that
pure samples can be obtained in the phosphorescent form. Various
attempts were made by us to prepare zinc sulphide by different
methods in order to determine the phosphorescence of samples
produced in different ways.

Ordinary precipitated zinc sulphide shows no trace of phos-
phorescence. Heat is necessary in order to produce the
phosphorescent condition, from which it may be deduced that the
physical nature of the sulphide (amorphous, semi-crystalline, or
crystalline) has a considerable bearing on the occurrence of the
property in question. Working on this idea, several other
methods of obtaining zinc sulphide were tried. If the calculated
quantities of sulphur and zinc are used as a "thermite" mixture,
deflagration occurs, and the zinc sulphide thus produced shows in
part a considerable power of phosphorescence. By conducting the
operation in a roomy vessel, the volatilised zinc sulphide is
separated into various sections lying on circles of different radii
with the crucible in the centre, and it is found that the power
of phosphorescence differs from circle to circle. The method, how-
ever, was of little practical value, owing to the fact that the size
of the crucible charge had an influence on the temperature attained
during the deflagration, so that standardisation was difficult. Also
no accurate measurements of temperature could be made, so that
it was impossible to guarantee an exact reproduction of the
experimental conditions. A further set of experiments was made

by heating zinc in a crucible and adding excess of sulphur; but here again the difficulty of exact reproduction of the experimental conditions vitiated the value of the method, and the results were not promising, although specimens of phosphorescent zinc sulphide were obtained in this manner. Similar drawbacks attended the addition of zinc to boiling sulphur and the interaction of zinc oxide and sulphur. The production of zinc sulphide by allowing zinc vapour and sulphur vapour to interact suffered from a similar defect, as the heat of reaction in this case is incapable of being regulated, and in addition the method is troublesome. Experiments were also made with the electric arc as heating agent, but with the same lack of definite success.

In general, we found that pure zinc sulphide is capable of giving rise to phosphorescence; but the effect is not a very marked one, and is not comparable with the phosphorescence obtained in the ways which will be dealt with later in the present paper.

II. *The Influence of Small Quantities of Impurities.*—Here again the literature is very confusing, as some authors describe certain impurities as being advantageous, whilst other investigators mention the same impurities as having a deleterious influence. From our own results we are inclined to believe that these contradictory data arise from the fact that different workers used different temperatures, and that the impurity played less part in the matter than has been supposed. All that can be said with certainty is that certain impurities, such as iron, seem to inhibit the power of phosphorescence to a great extent, whereas other admixtures, such as common salt, increase the phosphorescent effect. A rough empirical rule is that impurities of metals which give black sulphides seem to exert a deleterious effect on the phosphorescence of zinc sulphide. This rule, however, requires modification in some respects when the influence of temperature is considered, as will be seen later. It may be taken as proved that impurities do influence the phosphorescence phenomena, and that the amount of impurity required is extremely small.

III. *The Manner in which the Impurities are Introduced into the Zinc Sulphide.*—Fixed quantities of a given impurity may be introduced into a given sample of zinc sulphide by one of three methods. In the first place, the precipitated zinc sulphide may be mechanically mixed with the impurity before heating takes place; secondly, the precipitated zinc sulphide may be washed with a solution containing the impurity, and the material may then be dried in the steam-oven before heating, so that a certain amount of the impurity adheres to the particles of zinc sulphide; or, thirdly, the impurity may be placed in the solution of a zinc

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salt and the admixture obtained by precipitating the zinc sulphide
and neglecting to wash the precipitate after it has been produced.
All three methods give results. The first method is apt to pro
duce uneven preparations, owing to the mixture not being
sufficiently uniform; the second method is better, but the impurity
is only deposited on the outer edge of the flocky material, either
by adsorption or by mere mechanical deposit as the water is
removed. The third method insures that the impurity is occluded
in the precipitate, and therefore gives a much more uniform
result.

IV. *The Conditions of Precipitation.*—It occurred to us that
the precipitation of zinc sulphide from the solution of a zinc salt
was capable of taking place under two conditions: (*a*) when excess
of precipitant was present, and (*b*) when the zinc salt was in
excess, and it seemed possible that this might affect the character
of the final product. Experiments were therefore made in
some of which a zinc salt was added to excess of ammonium
sulphide, whilst in other experiments ammonium sulphide was
added to a solution containing excess of a zinc salt. When both
types of product were submitted to identical heating processes, it
was found that there was a marked difference in the phosphor-
escence produced. The greatest illuminating power was found in
the case where the zinc salt was present in excess; the other
samples (in which the whole of the zinc was precipitated) gave
much inferior results. This point will also be discussed later.
Its practical bearing was to give a preference to ammonium
sulphide over hydrogen sulphide as a precipitant, for in the case
of the former it was possible to break off the precipitating process
at any desired point, whereas with gaseous hydrogen sulphide it
was difficult to ensure that a fixed proportion of zinc was pre-
cipitated.

V. *The Treatment of the Wet Precipitate to Ensure Easy Filtra-
tion and Drying.*—The zinc sulphide precipitate is one which under
ordinary conditions entails considerable trouble in filtration, but
the following method was found to give good results. Zinc
chloride sticks were dissolved in water, giving as concentrated a
solution as possible. Ammonia was added until the precipitate
formed redissolved. The solution was then allowed to remain for
twenty-four hours, after which all precipitate (chiefly iron hydr-
oxide) was filtered off; the filtrate was diluted with water until
each litre contained a gram-atomic weight of zinc, and in making
up the solution 15 grams of sodium chloride per litre were added,
as it was found that the presence of this gave the best results.
Of this standard solution, 100 c.c. were raised to the boiling point,

then a given number of c.c. of a thousandth gram-molecular solution of some compound of the element used as impurity was added, and the zinc sulphide was at once precipitated with enough ammonium sulphide to bring down half the total quantity of zinc present. The quantities of "impurity" solutions used were 5 c.c., 10 c.c., 15 c.c., and 30 c.c. in the case of each element tested, so that four comparable results were obtained. In the case of basic elements, some soluble salt was employed, whilst for acidic elements the sodium salt was used wherever possible.*

After precipitation was complete, the boiling mixture was poured into an equal bulk of cold water containing 15 grams of sodium chloride per litre. Settling takes place rapidly, and the precipitate thus obtained is much more readily filterable than the ordinary material. After filtration, the material (without washing) was dried in a steam-oven, ground to fine powder, sieved through muslin, and was then ready for heating.

VI. *Effect of Temperature on the Production of Phosphorescent Zinc Sulphide.*—Two factors enter into this problem: (*a*) the temperature to which the sulphide is heated, and (*b*) the duration of the heating process. In order to obtain comparable results, we utilised an electric furnace with a thermo-couple, and in this way we were able to repeat our experimental conditions with a high degree of accuracy. Our first series of results was obtained by heating the prepared sulphide in a porcelain crucible for an hour and a-half in the electric furnace at a temperature of 650°. The material of the crucible may possibly exert a certain amount of effect, but graphite crucibles, which were tried, were found to be inconvenient from more than one cause, and we experienced no difficulties in using porcelain ones. The results obtained with porcelain crucibles will be given in Section VII.

Further investigation showed that, speaking generally, there are three grades of temperature which may be employed. Below 650° even prolonged heating produces only poor phosphorescent effects in the sulphide. Between 650° and 900° the results are much better, whilst heating for any length of time at 1100° produces very poor specimens. An examination of the samples obtained under these three conditions proved that the material produced below 650° was viscous and amorphous, that obtained between 650° and 900° was semi-crystalline under the microscope, whilst the substance produced at 1100° was purely crystalline. Of course, the change from semi-crystalline to crystalline material is to some

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* We were much indebted to Professor G. G. Henderson, F.R.S., who kindly furnished us with specimens of some of the rarer elements to complete the series.

extent dependent on the period of heating, some quite crystal-
line material being obtained by prolonged heating at 900°, whilst
semi-crystalline substances can be produced by a few minutes'
heating at 1100°.   For ordinary working purposes, however, it
was found that half an hour was the shortest interval of heating
which could be usefully employed, as less than this entailed
trouble with the exact regulation of the furnace after it had been
opened to admit the samples, and concordant results were not easy
to obtain.   Thus it may be taken that the best phosphorescent
samples are produced by heating to some temperature between
650° and 900° for a time not exceeding an hour and a-half.

Our next set of experiments was directed to testing whether the
phosphorescence was due to a state of strain being set up in the
crystalline structure of the sulphide, as this seemed possible from
a consideration of the results just described.   We therefore carried
out a series of experiments concerning the effect of quenching the
heated sulphide in various liquids.   Water, we found, gave poor
results, especially with material heated at a low temperature, as
deliquescent substances were present which had some influence on
the process.   Experiments with organic liquids, such as chloro-
form, carbon tetrachloride, and paraffins, gave better results; but
the process set up charring in the liquid, with the result that the
zinc sulphide was rendered dirty in parts.   We therefore aban-
doned this line of investigation.

Up to this point we had proceeded on the assumption that the
material should be screened from the air while being heated, and
had conducted all our experiments in tightly closed crucibles; but
as we wished to adopt a new system of sampling, we tested if any
difference in the product could be detected if the crucible was left
open or was kept tightly closed.   It appears that no appreciable
advantage is gained by the exclusion of air.   Samples in open
crucibles and others in closed crucibles gave very similar results.

This opened up a new possibility, and we proceeded to deter-
mine the exact period of heating which gave the greatest phos-
phorescent effect when the final product was illuminated by light.
A large crucible was filled with material and placed in the furnace,
already heated to a fixed temperature.   Samples were withdrawn
at fixed intervals of time, and were tested for light effect by cool-
ing and exposing them to daylight.   Thus we were able to trace
the maximum point of illumination and repeat our experimental
conditions at other times with certainty.

VII. *The Methods of Testing the Final Product.*—Phosphor-
escence may be excited in zinc sulphide in four different ways:
by light, by X-rays, by cathode rays, or by Becquerel rays from

radioactive substances. It will be necessary to consider these separately.

In order to test the relative brightness of phosphorescence under the action of light, a standard sample was chosen which showed a brilliant illumination after a brief excitation. The substance actually used was a zinc sulphide containing vanadium (30 c.c. of $M/1000$-sodium vanadate in 100 c.c. of M-zinc solution containing 1·5 grams of sodium chloride before precipitation) which had been heated for an hour at 750°. Any sample which, when submitted to the light test, gave an illumination equal to this was reckoned as Class A. The Class B standard was made up by mixing 0·5 gram of the vanadium standard mixed with 0·75 gram of precipitated (unheated) zinc sulphide, whilst the Class C standard consisted of 0·5 gram of the vanadium standard mixed with 2 grams of precipitated zinc sulphide. The illumination was made in the dark-room by means of a fixed length of magnesium ribbon. The estimation of intensity is at best only a rough one, as owing to the evanescence of the phosphorescence it is impossible to carry out exact photometric measurements. The results are shown in the accompanying tables in the columns A, B, and C. A cross ($+$) in the column indicates that the sample had a corresponding phosphorescence.

With regard to X-rays, the same standards were utilised, and each sample of zinc sulphide was compared by placing it on a card along with three standards and estimating the luminosity when submitted to the action of X-rays generated from an X-ray bulb below the card. In this case, also, the estimates of luminosity are necessarily rough. The results are shown by asterisks in the table.

Turning next to the excitation by means of cathode rays, the apparatus employed was simple. A tube in the form of an H had the disk-shaped cathode and anode sealed into the upper ends of the vertical tubes of the H, one in each. The bottom of the H-tube, opposite the cathode, was furnished with a ground stopper bearing on its upper surface a mica disk, which was kept well above the ground portion of the glass by being mounted on a glass rod or tube. The standard substance was placed on the mica plate along with the specimen to be compared, and the whole vessel was exhausted.

In order to differentiate between the sensitiveness of the various specimens, the number of strokes of the Töpler pump used throughout the experiments was employed, and these numbers are given in the following table. The readings "Green," "Blue," and "Yellowish-green" indicate the tint of the phosphorescence

shown. In the column headed "First response" is given the number of strokes of the pump necessary to produce the first faint indications of phosphorescence in the samples under investigation. The column headed "First brightness" indicates the number of strokes of the pump necessary to produce an appearance of internal glow in the samples. The column headed "Intensity" refers to the appearance of the illumination after the vacuum has been made as high as possible with the pump. Intensity I implies that the substance glows steadily, but with no marked brilliancy. Intensity II indicates that when the current is first applied, the substance exhibits a momentary flash and then dies down to a state similar to Intensity I. Intensity III covers the case in which the first flash is not momentary, but lasts for a short period—some seconds at least. Intensity IV represents a state in which the sample shows a much stronger illuminating power than the others, although after a minute or so of bombardment it declines slightly in lustre. Intensity V indicates that the substance shows an illumination like that of IV, but that the fatigue effects do not set in so markedly.

TABLE I.

Results for Samples Heated for an Hour and a-half at 600°.

Substance added to 200 c.c. N–Zn.	First response.	First brightness.	Green.	Blue.	Yellowish-green.	Intensity.	A.	B.	C.
15 c.c. $M/1000$-Li ...	7	7		10		II		*	+
30 ,, ,, ...	5	5	5	10		II		*	+-
5 c.c. $M/1000$-K ...	3	6	8			II		*	-|-
10 ,, ,, ...	3	6	6	8		II	*		-|-
30 ,, ,, ...	3	6	8			II	*		
5 c.c. $M/1000$-Rb ...	4	5	5	8		II	*		-|-
10 ,, ,, ...	4	5		8	5	II		*	-|-
15 ,, ,, ...	5	7	7	8		II		*	-|-
30 ,, ,, ...	4	5		8	5	II		*-|-	
5 c.c. $M/1000$-Cs ...	8	9	9	12		II		*	
10 ,, ,, ...	7	8	8	12		II		*	
15 ,, ,, ...	6	7	11	12		II		*	
30 ,, ,, ...	5	5	5	12		II		*	-|-
5 c.c. $M/1000$-Gl ...	5	6	5	8		II		*	+
10 ,, ,, ...	5	5	3	8		II	*		-|-
15 ,, ,, ...	5	6	5	8		II		*	-|-
30 ,, ,, ...	4	5	4	8		II		*-|	
5 c.c. $M/1000$-Mg ...	11	11	11			I		*	-|-
10 ,, ,, ...	5	5	12		11	I		*	|
15 ,, ,, ...	7	7	11			I	*		+-
30 ,, ,, ...	5	5	11	12		I		*	

TABLE I. (*continued*).

Results for Samples Heated for an Hour and a-half at 600°.

Substance added to 200 c.c. N–Zn.	First response.	First brightness.	Green.	Blue.	Yellowish-green.	Intensity.	A.	B.	C.
5 c.c. M/1000-Ca ...	7	7	7	8		II		*	+
10 ,, ,, ...	6	6	6	9		II	*	+	+
15 ,, ,, ...	5	6	5	8		II	*		
30 ,, ,, ...	4	6	4	8		II		*+	
5 c.c. M/1000-Sr	8	9	8	9		II		*	+
10 ,, ,, ...	7	8	9	11		II		*	
15 ,, ,, ...	5	5	9	11		II		*	
30 ,, ,, ...	5	5	9	11		II	*		
5 c.c. M/1000-Ba ...	5	6	5	9		I		*	+
10 ,, ,, ...	5	5	5	9		I		*	+
15 ,, ,, ...	4	5	4	9		I		*	+
30 ,, ,, ...	4	5	4	8		I	*		+
5 c.c. M/1000-Cd ...	5	6	8	9		I	*		+
10 ,, ,, ...	4	5	5	8		I	*	+	
15 ,, ,, ...	6	6	8	9		I	+	*	
30 ,, ,, ...	5	5	5	8		I		*+	
5 c.c. M/1000-Hg ...	10	11		10		I			+*
10 ,, ,, ...	6	6	11	12		I		*	
15 ,, ,, ...	6	6	11	12		I			*
30 ,, ,, ...	5	5	5	11		I		*	
5 c.c. M/1000-B ...	6	7	6	9		II		*	+
10 ,, ,, ...	5	6	5	9		II		*	+
15 ,, ,, ...	6	7	6	9		II		*	
30 ,, ,, ...	5	6	5	9		II		*	
5 c.c. M/1000-Al ...	5	6	5	8		II		*	
10 ,, ,, ...	4	5	4	8		II		*	
15 ,, ,, ...	6	6	6	8		II	*		+
30 ,, ,, ...	5	6	5	7		II		*	+
5 c.c. M/1000-Y ...	6	9	9			II		*	+
10 ,, ,, ...	4	5	9			II		*	+
15 ,, ,, ...	8	9				II		*	+
30 ,, ,, ...	5	5	9			II		*	
5 c.c. M/1000-La ...	6	7	9		6	II		*	
10 ,, ,, ...	4	6	11			II		*	
15 ,, ,, ...	8	8	9		6	II		*	+
30 ,, ,, ...	4	6	12			II	*		+
5 c.c. M/1000-Tl ...	8	10		9		II			*
10 ,, ,, ...	5	5	9	10		II		*	
15 ,, ,, ...	5	5	9	10		II	*		
30 ,, ,, ...	5	5	9	10		II		*	
5 c.c. M/1000-In ...	5	6	5			II		*	+
10 ,, ,, ...	5	6	5	9		II		*	+
15 ,, ,, ...	6	6	6	9		II		*	+
30 ,, ,, ...	5	6	5	9		II		*	+

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TABLE I. (*continued*).

Results for Samples Heated for an Hour and a-half at 600°.

Substance added to 200 c.c. N–Zn.	First response.	First brightness.	Green.	Blue.	Yellowish-green.	Intensity.	A.	B.	C.
5 c.c. M/1000-C ...	8	8	8	10		I		*	+
10 ,, ,, ...	5	6	6	10		I	*		+
15 ,, ,, ...	7	8	7	9		I		*	+
30 ,, ,, ...	5	6	6	9		I		*	
5 c.c. M/1000-Si ...	6	8	6	9		II		*	
10 ,, ,, ...	5	7	5	10		II		*	+
15 ,, ,, ...	5	7	5	10		II		*	
30 ,, ,, ...	5	7	5	10		II			+*
5 c.c. M/1000-Ti ...	3	5	3	7		II		*+	
10 ,, ,, ...	5	5	5	7		II	*+		
15 ,, ,, ...	5	5	5	9		II	*	+	
30 ,, ,, ...	5	5	5	9		II	*	+	
5 c.c. M/1000-Zr ...	6	7		8		II		*+	
10 ,, ,, ...	4	5	4	8		II		*+	
15 ,, ,, ...	6	7		8		II	*	+	
30 ,, ,, ...	4	5	4	8		II	*+		
5 c.c. M/1000-Ce ...	5	6	5	9		II		*	+
10 ,, ,, ...	5	6	5	9		II		*+	
15 ,, ,, ...	6	6	6	9		II		*+	
30 ,, ,, ...	5	6	5	9		II		*	
5 c.c. M/1000-Sn ...	9	10	11	11		II		*	+
10 ,, ,, ...	7	7	11			II		*⫶	+
15 ,, ,, ...	4	5	11			II		*	+
5 c.c. M/1000-Pb ...	3	5	5	8		III		*	⫶
10 ,, ,, ...	5	5	5	8		III		*	⫶
15 ,, ,, ...	4	5	4	8		III		*	⫶
30 ,, ,, ...	4	5	4	7		III		*⫶	
5 c.c. M/1000-Th ...	5	6	7	9		II			*+
10 ,, ,, ...	5	6	5	11		II		*⫶	
15 ,, ,, ...	8	9		11		II		+	*
30 ,, ,, ...	5	9	5	11		II			*⫶
5 c.c. M/1000-N ...	5	6	5	9		III		*+	
10 ,, ,, ...	4	6	4	9		III	*	+	
15 ,, ,, ...	4	6	9			III		*⫶	
30 ,, ,, ...	5	6	5	9		III		*	+⫶
5 c.c. M/1000-P ...	3	5	9	10		III		*+	
10 ,, ,, ...	3	5	5	9		III	*	+	
15 ,, ,, ...	7	9	7	9		III		*	+
30 ,, ,, ...	3	5	9	10		III	*	+	
5 c.c. M/1000-V ...	4	5	4	10		II		*	+
10 ,, ,, ...	4	5	4	10		II			*
15 ,, ,, ...	4	5	4	10		II		+	*
30 ,, ,, ...	5	10	5	11		II			

TABLE I. (*continued*).

Results for Samples Heated for an Hour and a-half at 600°.

Substance added to 200 c.c. N–Zn.	First response.	First bright-ness.	Green.	Blue.	Yellow-ish-green.	Inten-sity.	A.	B.	C.
5 c.c. $M/1000$-As ...	5	5	5	11		II		*	+
10 ,, ,, ...	5	5	5	11		II		*·+	
15 ,, ,, ...	6	7	6	11		II			*
30 ,, ,, ...	6	7	6	11		II			*
5 c.c. $M/1000$-Sb ...	4	5	4	10		II		*·+	
10 ,, ,, ...	6	9	6	13		II	*·		+
15 ,, ,, ...	4	5	4	13		II		*	+
30 ,, ,, ...	4	5	4	10		II		*·+	
5 c.c. $M/1000$-Bi ...	9	9		10		II			*
10 ,, ,, ...	4	5	4	10		II		*·+	
15 ,, ,, ...	5	6	5	9		II			*
30 ,, ,, ...	4	5	4	10		II		*	
5 c.c. $M/1000$-Cr ...	8	8	8	14		I		*	+
10 ,, ,, ...	3	6	3	15		III		+	*
15 ,, ,, ...	6	10	6	14		I			*·+
30 ,, ,, ...	5	7	5	14		I			*
5 c.c. $M/1000$-Ms ...	5	7	5	11		I		*	+
10 ,, ,, ...	5	5	5	11		I	*		+
15 ,, ,, ...	5	6	5	11		I	*		+
30 ,, ,, ...	5	6	5	11		I		*	+
5 c.c. $M/1000$-W ...	5	5	5	11		I			
10 ,, ,, ...	5	5	5	11		I			
15 ,, ,, ...	7	7		11		0			
30 ,, ,, =	8	8		11		0			
5 c.c. $M/1000$-U ...	11	12	11	14		I		*	
10 ,, ,, ...	6	7	6	13		I			*
15 ,, ,, ...	5	5	5	14		I			*·+
30 ,, ,, ...	5	5	5	14		I		*	
5 c.c. $M/1000$-Se ...	4	6	4	9		II	*		+
10 ,, ,, ...	5	5	5	8		II	*		+
15 ,, ,, ...	5	6	5	9		II		*	+
30 ,, ,, ...	5	7	5	9		II		*	
5 c.c. $M/1000$-Te ...	5	9	5	11		II		*	+
10 ,, ,, ...	3	5	3	11	5	III		*	
15 ,, ,, ...	3	5	3	11	5	II			*
30 ,, ,, ...	3	5	3	11	5	II		*	+
5 c.c. $M/1000$-Mn ...	6	5	6			II			*
10 ,, ,, ...	5	3	6			II		*	+
15 ,, ,, ...	5	3	5			II	*	+	
30 ,, ,, ...	4	3			4	II		*	+
5 c.c. $M/1000$-Br ...	8	8		20	8	I		*	
10 ,, ,, ...	8	10	8	20		I		*	+
15 ,, ,, ...	7	8	7	20		I		*	+
30 ,, ,, ...	5	6	5	20		I	*	+	

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TABLE I. (continued).

Results for Samples Heated for an Hour and a-half at 600°.

Substance added to 200 c.c. N–Zn.	First response	First brightness	Green	Blue	Yellowish-green	Intensity	A	B	C
5 c.c. M/1000-I	6	6	6	14		II		*	+
10 ,, ,,	5	6	5	14		II		*	+
15 ,, ,,	5	6		14	6	II			*
30 ,, ,,	5	6	5	14		II		*	+
5 c.c. M/1000-Fe	12	12	12			I		*	
10 ,, ,,	5	5	12	14		I	*		+
15 ,, ,,	6	7	12	14		I		*	+
30 ,, ,,	4	5	4	12		I	*		+
5 c.c. M/1000-Co	12	13			12	I			
10 ,, ,,	13	13			13	I			
5 c.c. M/1000-Ni	6	7	7	15		I			*+
10 ,, ,,	5	7	7	15		I		*	
15 ,, ,,	5	7	7	15		I		*	
30 ,, ,,	15	15		15		I			*
5 c.c. M/1000-Ru	6	7	6	12		II		*+	
10 ,, ,,	5	5	11	12		II	*		+
15 ,, ,,	6	7	6	12		II		*+	
30 ,, ,,	5	6	11	12		II			*
5 c.c. M/1000-Rh	8	9		9		II		+	*
10 ,, ,,	5	5	5	11		II		+	*
15 ,, ,,	6	8	6	10		II		+	*
30 ,, ,,	4	5	4			II			*+
5 c.c. M/1000-Pd	6	9	6		8	I		*	
10 ,, ,,	8	10	8		9	I		*	
15 ,, ,,	6	9	6			I	*		
5 c.c. M/1000-Os	7	11		10		II			*
10 ,, ,,	7	11		10		II			*
15 ,, ,,	7	10		10		II			
30 ,, ,,	7	12		10		II			
5 c.c. M/1000-Ag	4	5	5	6		II		*	+
10 ,, ,,	4	5	5	6		II		*	+
15 ,, ,,	5	5	5	6		II		*	+
30 ,, ,,	4	5	5	6		II		*	+
5 c.c. M/1000-Ta	4	6	4	7		II		*	+
10 ,, ,,	4	6	4	7		II	*+		
15 ,, ,,	5	6	6	7		II		*	+
30 ,, ,,	4	6	4	7		II		*	+

In the following samples, 30 c.c. of M/1000-impurity were added to 200 c.c. of M-zinc, and the sample was heated for half an hour at the temperature mentioned.

TABLE II.

Temperature and impurity.	First response.	First brightness.	Green.	Blue.	Yellowish-green.	Intensity.	A.	B.	C.
*600–650°	5	6	5	7		II		*+	
650–700°	2	5	2	7		II	*+		
700–750°	2	5	2	7		IV	*+		
750–800°	2	5	2		6	V	*+		
800–950°	4	6	4		6	III		*+	
V 650–700°	4	4	4	6		I	*+		
700–750°	1	4	1	6		II	+	*	
750–800°	1	5	6	8		IV	*+		
800–850°	1	5		8	1	IV	*+		
Ti 600–650°	6	6	6	8		II		*+	
650–700°	3	7	3	8		II	*	+	
700–750°	3	7	8	9		IV	*+		
750–800°	7	7			7	IV	*+		
Au 650–700°	3	5	5	8		IV	*+		
750–800°	3	5	5		7	III	*+		
Zr 600–650°	5	5		6		II		*+	
650–700°	1	4	5			III		*+	
700–750°	1	4	1			IV	*+		
750–800°	3	5	3		5	III	*+		
Th 600–650°	5	6	5	6		II		*+	
650–700°	1	6	6	9		III	*+		
700–750°	2	6	6			IV	*+		
750–800°	5	6	7			III	*+		
Zr 600–650°	5	5	5	6		II		*	+
& 650–700°	2	5	7			III		*+	
Mn 700–750°	1	5	6			V	*	+	
750–800°	4	6			4	IV	+	*	
Zr 600–650°	4	5	4	6	5	II	*		+
& 650–700°	4	5	4	6	5	II	*+		
Ti 700–750°	3	5	6		5	IV	+	*	
750–800°	4	5	5	6		V	*+		
Mn 600–650°	5	6	5			II		*	
650–700°	5	5	5			II		*	+
700–750°	1	5	1		8	IV	*+		
750–800°	1	5	1			IV	*	+	
800–850°	2	6	2		6	IV	*	+	
850–900°	2	5	2			III	*	+	
900–950°	2	4				III	*	+	

* To these five samples no impurity was added except sodium chloride.

We have given no measurements made with radium for two reasons. In the first place, owing to the use of radium paint at the present time for military purposes, it seems undesirable to offer any such results just now. Secondly, we did not carry out such complete measurements with radium as we did with other sources

of energy. It is desirable to state, however, that the results obtained with radium do not in any way concord with those observed with light, etc., although our earlier investigations led us to believe that there was a close similarity in effect between the response of zinc sulphide to radium and to light. Fuller examination of the material at our disposal has shown us, however, that there is no parallelism between the two actions. The effect of the α-particle bombardment is apparently quite incapable of being predicted from the results obtained from other sources of excitation.

As it may assist others who are working in this region of the subject, we may mention two methods whereby the influence of radioactive materials on phosphorescence may be tested without loss of the radioactive substance. The first of these, which was devised by the late Sir William Ramsay, consists in coating one side of a microscope cover-glass with a known quantity of radium, covering this with a protective film, and then placing the cover-glass (radium side downwards) on the surface of the preparation to be examined. The resulting illumination is observed through the cover-glass, and by using cover-glasses of equal surfaces on which different quantities of radium have been deposited, a rough estimation may be made of the relative luminosities of two samples of zinc sulphide. The method of preparing the cover-glasses is simply to allow a fixed number of drops of a solution of a radium salt of a known strength to fall on the cover-glass surface, then heat the glass in an oven until the water evaporates, taking care to see that an even deposition results. When the film is dry, it is covered with a thin film of " dope " or of collodion, which has little effect on the radiation.

In order to estimate the effect of α-rays, apart from the other constituents of the Becquerel rays, the following method may be employed, for which we are indebted to Dr. A. Fleck. A quill tube of glass is sealed at one end, and into it are introduced various samples of sulphide which it is desired to compare. Each sample is loosely packed, and is separated from its neighbours by a loose wad of cotton-wool. The tube is then pumped out and niton is introduced into it; the free end is then sealed. In this way, a rapid estimate of the effect of the α-ray may be obtained.

VIII. *The Influence on Phosphorescence Produced by Impurities in Large Quantities.*—Hitherto we have dealt with the effects produced by impurities present in extremely small quantities, but it seemed necessary to examine also the results obtained when much greater quantities of impurities were added to the zinc sulphide. It has been well known for a considerable time that

zinc sulphide containing an admixture of sodium chloride gave results very much superior to those observed when pure zinc sulphide was employed. In the ordinary method of preparing zinc sulphide (precipitation of ammoniacal zinc solutions), it is clear that the unwashed precipitate must contain a considerable amount of adherent or occluded ammonium chloride, so that in the experiments described above it is clear that our specimens before heating must have been mixed with the chlorides of sodium and ammonium. In order to determine whether the presence of these compounds had any effect on the ultimate product, we examined a series of samples in the following manner. The precipitation, drying, and powdering were carried out as usual, and then each sample was divided into two parts. One of these was thoroughly washed to remove any soluble impurity. whilst the other was left untreated. Both samples were then heated alongside each other in the furnace, and it was found that whilst the "unwashed" sample gave the usual result, the "washed" sample lagged much behind it in phosphorescing power. From this it follows that the presence of the two impurities had a considerable effect on the phosphorescence of the final product. To make sure of this point, we prepared fresh samples of zinc sulphide, precipitated and dried as before. Each sample was then washed thoroughly with water to remove the impurities, and the washed precipitate was divided into two parts. One part was left without further treatment, whilst the other was soaked for a time in a solution of sodium chloride. Both were then dried in the same oven and heated side by side in the same furnace. It was found that the "washed" sample gave a much feebler phosphorescence than the other which had been again rendered impure, from which it must be deduced that the presence of sodium chloride has a considerable influence on the production of phosphorescence. Similar results were obtained by mixing the washed material with ammonium chloride, but the resulting compounds were not so good as those made with sodium chloride.

Now when zinc sulphide is heated to a high temperature in the presence of sodium chloride, it is natural to expect that interaction between the two compounds will take place, resulting in the formation of zinc chloride and sodium sulphide. That this view is correct was shown to us by the emission of fumes of zinc chloride from the electric furnace while these samples were being heated, and also by the deliquescent nature of several samples which had not been heated high enough to cause the complete volatilisation of the zinc chloride. This suggested to us that the presence of zinc chloride is to some extent necessary during the heating of the

material if good phosphorescent samples are to be obtained. It then occurred to us that this was sufficient to explain the results mentioned in Section IV., when we found that precipitation in presence of excess of zinc chloride gave good results, whilst precipitation in presence of excess of ammonium sulphide gave much feebler preparations. In the former case, a certain amount of zinc chloride will adhere to the sulphide, which cannot happen in the second case.

In order to test this point more rigidly, we prepared a solution of zinc acetate and used it as a source of zinc sulphide, thus excluding the presence of any chloride. These sulphide samples showed very poor phosphorescence, a fact which seems to strengthen our views.

It will be recalled that in an earlier section of this paper the rough rule was given that an impurity giving rise to a black sulphide was deleterious in its effect on the phosphorescence, but that there were exceptions to this rule. The following will make the point clearer. When an M-zinc solution containing $M/100$ of a bismuth salt and 15 grams per litre of sodium chloride is precipitated with half the requisite amount of ammonium sulphide necessary to bring down all the zinc, the precipitate is dark grey, and when dry is almost brown. When heated at 800° for an hour, this material yields beautiful specimens of clear yellow zinc sulphide which show a fair amount of phosphorescence, although not so good as many samples which were obtained by other methods. The reason of this obviously lies in the fact that the bismuth sulphide, in the presence of excess of sodium chloride, forms bismuth chloride, which is volatilised away during the process of heating. None the less, it has some action on the end-product. This leads to the conclusion that phosphorescent power is connected in some way with a physical state, and not so markedly with chemical change. In volatilising from the inside of the particles of the zinc sulphide precipitate, the bismuth chloride may have broken them up into small aggregates, and its influence may have been due to this cause. The volatilisation of zinc chloride from a preparation would have a similar effect. We do not wish to lay too much stress on this point, as it requires further investigation, but it seems to deserve notice, as it points to the fact that the influence of an impurity may not necessarily depend on its presence throughout the whole course of the preparation.

We have already directed attention to the fact that the best samples of phosphorescent zinc sulphide were those which exhibited a semi-crystalline structure under the microscope, so that there appears to be little doubt that there is an intimate connexion

between physical state and power of showing phosphorescence after excitation by light.

With regard to the colour effects produced by the admixture of small quantities of impurities, these are, generally speaking, very feeble. Only in the case of manganese is there a really marked change in the tint. We have been able to confirm the observation of Hofmann and Ducca (*Ber.*, 1904, **37**, 3407) that zinc sulphide, prepared from a solution containing M-zinc, 15 grams of sodium chloride per litre, and $M/100$ of a manganese salt, shines with a beautiful orange-golden tint, and also that this kind of zinc sulphide exhibits a most striking triboluminescence. In the latter property it far exceeds anything which we have seen in this field, and might almost be capable of utilisation as a lecture experiment.

As to the effect of temperature on the colour of zinc sulphide, we find that specimens which have been prepared at 650° are blue in phosphorescence, whilst high temperatures lead to greens and even yellows.

Another point which seems to indicate that physical condition is an important factor in conditioning phosphorescence is found in the following facts. A specimen of strongly phosphorescent zinc sulphide was washed with water and carefully dried. When its phosphorescent power was compared with that of the untreated material, it was found that the washing process had greatly decreased the brilliancy of the phosphorescence. Similar results were observed when 90 per cent. alcohol was used instead of water, although in this case the diminution in the activity of the sample was much less than in the case of water. Washing with ether appears to have less influence even than when alcohol is used. The ether employed was not absolutely dry.

This suggests that phosphorescent zinc sulphide contains some material soluble in water and alcohol which increases the phosphorescent power of the substance. Possibly the masses of zinc sulphide are covered with a layer of zinc chloride so thin that no appreciable deliquescence is noticeable, and this soluble material may be setting up a strain upon the enclosed sulphide which renders it more capable of showing anomalous effects when subjected to the action of light. The removal of the skin of foreign material by the action of water would release the strain, and hence cause a diminution of the phosphorescent power of the contained sulphide.

In confirmation of this idea, the following fact may be quoted. When a strongly phosphorescent specimen of zinc sulphide is ground in a mortar, or even rubbed well between the fingers,

it loses a considerable portion of its phosphorescing power.* Here again it is clear that any surface film would be broken up or cracked, and that the internal portion of the material would be released from strain. In any case, it is evident that the action must be a mechanical one not concerned with the chemical nature of the sulphide.

Some other points that have arisen during the work may be noted here. We have been able to confirm the statement of Becquerel and others with regard to the behaviour of zinc sulphide when cooled. If two specimens of the same sample are chosen, and one cooled in liquid air whilst the other is kept at the ordinary temperature, it is found that if they are simultaneously excited by a magnesium flash both of them will glow with almost equal brilliancy, but if the cooled sample is withdrawn from the liquid air, its phosphorescence increases in intensity as the temperature of the sample rises until at the ordinary temperature it much exceeds that of the uncooled sample. This phenomenon might also be brought into line with the idea of a foreign coating on the surface of the particles of sulphide, as differential cooling would increase the strain, and hence increase the anomalous light effect.

Another observation made by us tends to show that this effect of temperature is a general one. In the course of taking samples from highly heated zinc sulphide in the electric furnace, we noted that if a sample were exposed to light while it was very hot, it did not appear to become sensitised to any extent. On cooling, it became capable of sensitisation, and glowed well in the dark after exposure to light. Further, if this still glowing sample were thrown back on the top of the remaining zinc sulphide in the hot crucible, it immediately phosphoresced brilliantly, although the light emission was only of brief duration. It therefore seems to be a general rule that substances at low temperatures can take in an extra store of light-energy, which they throw out rapidly as the temperature rises, the light-emission at temperatures of 800° to 1000° being a mere brilliant flash.

Another point of interest is the phenomenon to which allusion has already been made, namely, the brilliant flash shown by certain specimens under the first impact of the cathode ray, and the subsequent "fatiguing" of the material so that the phosphorescence diminishes after the flash to a feebler glow. This flashing effect can be repeated at will by simply allowing the discharge to cease for a minute or two; on turning on the current again, the same

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* The triboluminescence of zinc sulphide with manganese also decreases with continued rubbing. At first mere pressure on the substance suffices to yield a flash, but soon hard grinding in a mortar is necessary.

process of flash and fatigue is visible. The flash is in some cases quite bright enough to throw a shadow in an ordinary room where no precautions have been taken to surround the apparatus with a screen.

One further matter in connexion with the cathode discharge may be mentioned. If the cathode ray is allowed to play upon a specimen of zinc sulphide for a few minutes, it is found, after the current is interrupted, that the surface of the material is discoloured; in some cases the original, nearly white sulphide becomes covered with a grey (or in some cases brown) film. So long as the specimen is kept in the cathode tube, even after being kept for a day, this tint remains fixed, but a few minutes' exposure to air suffices to bring it back to the original white or yellow colour of the sulphide. A similar effect is noticed in specimens of zinc sulphide which have been exposed to the influence of niton. Samples which originally were clear lemon-yellow in tint become converted into brown or dove-coloured powders, and it was found that hand-in-hand with this change came an alteration in the tint of the phosphorescence itself. The original green hue gave place to a more blue light as the powder changed from yellow to a slate tint. Heating the material in the tube had no effect, so far as the restoration of the original colour of the powder was concerned.

Summarising the foregoing, the following points appear to be definitely established. Pure zinc sulphide prepared in various ways can be obtained in a phosphorescent condition. The addition of certain impurities has a marked effect in some cases, and this effect may take the form of inhibiting the phosphorescence (as with iron) or altering its tint (as is the case with manganese). The presence of a chloride, whether it be zinc chloride or the chloride of some other element, has an advantageous influence. The factor which has the greatest influence, however, is the temperature to which the zinc sulphide is heated. This temperature effect can be varied within limits; thus a sample heated for a very short time to a high temperature will give effects similar to those observed in another sample heated for a longer time at a lower temperature, provided that the lower temperature is not less than about 750°. Washing, rubbing, or disturbing the final product in any way tends to diminish its phosphorescent power. Amorphous sulphide does not phosphoresce, nor does purely crystalline sulphide show such good phosphorescence phenomena as samples which contain semi-crystalline material. Specimens made from zinc salts not containing chlorides do not show such brilliant phosphorescence as those produced in the presence of chlorides.

With regard to the ultimate cause of the phosphorescence of
zinc sulphide, it is at present impossible to go further than the
statement that the salt in some manner acts as a reservoir of
energy which it can emit in the particular form of light vibra-
tions, but the foregoing data appear to throw some light on the
conditions governing the process.

In the first place, the influence of temperature on the storing
and emission process deserves attention.   It may be taken as
proved that the colder the zinc sulphide, the more energy it is in
a condition to absorb, but this absorbed energy must have a short
wave-length if it is to be converted into phosphorescence.   This is
shown by the fact that a sample of sulphide cooled in liquid air
in the dark does not emit light on being raised to the ordinary
temperature unless it has already been sensitised by the action
of light.   Further, a specimen which is sensitised while at a
temperature of, say, 400°, shows no phosphorescence to the eye,
but if it is rapidly heated to 800° it phosphoresces brilliantly,
although transiently, evidently giving up its store of accumulated
energy very rapidly at the higher temperature.   A similar pheno-
menon is noticeable in the case of the specimens cooled in liquid
air; when they are taken out of the cooling vessel, their phosphor-
escence becomes more and more brilliant, reaches a maximum, and
then dies down quite appreciably.   This suggests some analogy to
the flash obtained in the case of the first application of the cathode
discharge to certain specimens of zinc sulphide, and it may be
possible that this "flash" is produced by the sudden local rise of
temperature on the surface of the specimen, caused by the impact
of the cathode discharge, which is known to give heating effects.

These phenomena point to the fact that phosphorescence is much
influenced by physical conditions, and cannot be regarded as
entirely due to the chemical nature of the phosphorophore.   Other
data give similar indications.   Thus it has been established that
the strongest phosphorescence is observed in specimens which are
just on the border between the amorphous and crystalline condi-
tions, and that this state can be attained either by heating for a
very short period at a high temperature or for a longer time at
lower temperatures.   Again, the fact that washing diminishes the
brilliancy of the phosphorescence in the final product points to
the probability that some material is present which has a strong
influence on the phenomenon.   Since crushing, grinding, or
rubbing of the final product also decreases its phosphorescent
power, it seems reasonable to connect the two phenomena by the
assumption that the supposed impurity forms a skin over the
particles of the sulphide, which skin is removed by washing or

cracked by grinding. If the power of phosphorescence were governed entirely by the chemical character of the sulphide, such phenomena would be inexplicable, but if it is assumed that zinc sulphide alone possesses a feeble power of phosphorescence which can be enhanced by the operation of outside influences, the whole series of data fall into line.

With regard to the nature of this supposed impurity, the experiments given above throw some light on the problem. In the first place, it has been shown that the presence of sodium chloride during the preparation of the sulphide has a marked enhancing effect on the light-emission. Zinc chloride also assists the phosphorescence of the final product. This indicates that the chloride ion may lie at the root of the matter, and this idea is confirmed by the observation that sulphides prepared from zinc solutions containing no chloride have much less phosphorescing power than those produced in the presence of chlorides, as well as by the fact that large quantities of ammonium chloride in the solution increase the light emission of the final product. It may be suggested that the action of the traces of chloride is of the following nature. When the impure sulphide is heated, the chloride reacts with it and produces a surface film of zinc chloride on the sulphide, and this film, on cooling, may contract and produce a strained condition of the material within the film. The effect of additional impurities would be to influence the fusibility of the sulphide and chloride, and it may be in this action that the main influence of the impurities is to be sought. In any case, it seems reasonable to deduce that this film is brittle and soluble in water, as otherwise it is impossible to account for the phenomena observed in washing or grinding of the phosphorescent sulphide. Only one fact is unaccounted for by this hypothesis, namely, the alteration in colour of the emitted light which is observed when manganese is used as an impurity. All other impurities influence the phosphorescence tint but slightly, the range of colours extending from lemon tint to green and bluish-green, but in the case of manganese the emitted light is golden to orange, quite distinct from the usual appearance of zinc sulphide. In this case it is hard to avoid the conclusion that some chemical phenomenon must be concerned, but our experiments have thrown no light on its origin.

LX.—*Salts of Thiocarbamide.*

By AUGUSTUS EDWARD DIXON.

DURING the prosecution of a certain research, some salts of thio-carbamide have been isolated. As very few of such compounds appear to be known, except the nitrate (Emerson Reynolds, *Journ. Chem. Soc.*, 1869, **22**, 5) and the hydrochloride (Stevens, T., 1902, **81**, 80), mention may be made of those now obtained.

From the fact that the solubility of thiocarbamide in water is enhanced by the presence of strong acids, it is evident that salts are formed in solution. They are, however, markedly hydrolysed, and since, as a rule, they are freely soluble, whilst the parent base requires for dissolution at the ordinary temperature about nine times its own weight of water, their isolation in the presence of this solvent is frequently impracticable.

Thiocarbamide Hydrochloride.

To what Stevens (*loc. cit.*) has recorded in connexion with this substance, the following may be added.

Of the ready formed salt, 1·48 parts (= 1 part of thiocarbamide) required for dissolution 6·65 parts of water. When allowed to evaporate, the solution at first deposited thiocarbamide alone, this being accompanied later, when the bulk had considerably diminished, by crystals of the hydrochloride.

Also, when 1 part of thiocarbamide was treated with a prepared solution of hydrochloric acid (really 0·5 per cent. weaker than had been intended) dissolution required 7·15 parts, consisting of 0·45 part of hydrogen chloride and 6·7 parts of water. Thus, in the direct and in the reversed experiments, the end-systems were respectively :

$$(i)\ \ CSN_2H_4 : HCl : H_2O = 1 : 0·48 : 6·65 \text{ and}$$
$$(ii)\ \ CSN_2H_4 : HCl : H_2O = 1 : 0·48 : 6·70.$$
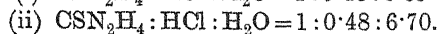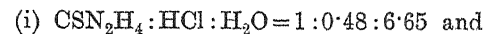
Obviously, these two were alike, the trifling excess of water in (ii) corresponding with the deficiency of hydrogen chloride in the pre-pared solution of hydrochloric acid; the action, therefore, is reversible.

By operating as follows, a 75 per cent. yield may be obtained of a salt that is practically pure. To every 10 grams of thiocarbamide 9 c.c. are added of ordinary concentrated hydrochloric acid (D, 1·16) ; the thiocarbamide is dissolved by warming the mixture, and hydro-gen chloride is passed in until distinct fuming is perceptible (during

the operation, a little hydrogen sulphide escapes). To prevent "setting," the solution, as it cools, should be well stirred; the crystals are now powdered if necessary, drained as far as possible by the aid of the pump, thoroughly washed with chloroform, pressed in folds of bibulous paper, and dried over sulphuric acid. Analysis of two different preparations gave:

Found: HCl = 32·40, 32·61. After recrystallisation from hydrochloric acid, 32·36.

CH_4N_2S,HCl requires HCl = 32·44 per cent.

It is possible, by reducing the proportion of concentrated hydrochloric acid, to increase the yield still further, but this is not desirable, for even with 8 c.c. per 10 grams of base the liquid, on cooling, sets to a mass so hard that it cannot easily be freed from the mother liquor.

In a dry atmosphere, at the ordinary pressure, the salt undergoes little change; a specimen kept for thirteen months over sulphuric acid was found at the end of that time to have lost only 0·7 per cent. of hydrogen chloride. At 15° it is twice as soluble as thiocarbamide, 1 part of the salt requiring about 4·5 parts of water; the solution, however, contains much of the total base as free thiocarbamide. Curiously, it is less soluble than the nitrate, this seeming paradox depending on the fact that it is more hydrolysed than the latter; hence, a larger amount of water is necessary to dissolve the resultant free thiocarbamide.

Fusion, which took place at about 136—137°, with the evolution of a trace of gas, was preceded by distinct softening; after recrystallisation from highly concentrated hydrochloric acid, the same behaviour was shown, except that the melting point was now 135—136°. No sign of change was perceptible when the salt was put into the apparatus at 103°.

Stevens found the substance to be fusible below 100°. To remove the mechanically adherent acid, he had washed the crystals with alcohol, a procedure likely to cause hydrolysis. On this point the following experiment was made: a quantity of the salt, having a primary melting point of 136—137°, was washed very rapidly, by the aid of the pump, with just enough strong alcohol to cover it; a portion, A, of the residue having been withdrawn, the remainder was again rapidly washed as before, leaving a twice washed material, B, the duration of each washing being about five seconds. Portion A softened gradually from 60° on, changing at 75° to an opaque paste which, by 112°, was transparent; portion B, placed in the apparatus at 85°, melted at once to a turbid liquid, becoming clear at 98°. Although the melting point is so strongly affected, the extent of hydrolysis caused by rapid washing cannot be very

great; for Stevens, who made several analyses, obtained quite satis
factory figures.

Another portion of the salt was heated at the fusion tempera-
ture for half-an-hour. The escaping gas consisted of hydrogen
chloride, with a trace of hydrogen sulphide; the residue, entirely
soluble in water, consisted principally of free thiocarbamide, together
with a little unchanged hydrochloride and enough ammonium thio-
cyanate (see Reynolds and Werner, T., 1903, **83**, 4) to give a well-
marked reddening with ferric chloride. No indication was
detected in the residue of the presence of an imino-base,
$NH_2\cdot C(:NH)\cdot SH$.

Although thiocarbamide is a diacidic base, yielding (see below)
the salts CSN_2H_4,H_2SO_4 and $CSN_2H_4,H_2C_2O_4$, no evidence has
been found that it can afford corresponding salts with monobasic
acids; for example, the dihydrochloride, $CSN_2H_4,2HCl$, is not pro-
ducible—or, at all events, was not detected—even in the presence of
a large excess of free hydrogen chloride. On the other hand, no
sulphate, $(CSN_2H_4)_2,H_2SO_4$, could be isolated.

Thiocarbamide and Sulphuric Acid.

When sulphuric acid was mixed with a saturated solution of
thiocarbamide in acetone, a colourless oil was precipitated, chang-
ing, when kept over sulphuric acid in a vacuum, to a white, crystal-
line substance, rapidly attracting moisture from the air.

Found (by titration): $H_2SO_4 = 55\cdot0$.

CH_4N_2S,H_2SO_4 requires $H_2SO_4 = 56\cdot3$ per cent.

This rather low figure was the best obtained, other preparations
giving lower values, the lowest of which was about 52 per cent.

When thiocarbamide was treated with enough 98 per cent. sul-
phuric acid to afford 1 molecular proportion of the acid, the base
soon dissolved, yielding a syrup, possibly the solution of the salt in
the small quantity of water present. This was at 20°; on cooling to
9°, the syrup changed to a white solid.

Thiocarbamide sulphate is soluble in glacial acetic acid, from
which it is precipitated by acetone or by chloroform in oily droplets,
which presently crystallise.

Thiocarbamide Nitrate.

Between the solubility of ready-formed thiocarbamide nitrate in
water and that of thiocarbamide in a dilute nitric acid having
about the concentration calculated from that solubility a disagree-
ment was found, the weights of water (for 1 part of thiocarbamide)
being 6·8 parts and 6·3 parts respectively. The variance is probably

due to a partial oxidation of the salt, during the process of drying, into the dinitrate of formamidine disulphide, $C_2S_2N_4H_6,2HNO_3$, a sparingly soluble compound, which decomposes rather easily, with the production of free sulphur. The nitric acid used in preparing the nitrate was previously swept by a current of air, and in these circumstances the salt—except as mentioned above—seemed tolerably stable. Curiously enough, when the nitric acid was previously boiled with carbamide, to remove every trace of nitrous acid, the nitrate prepared from it, as soon as it became dry in the desiccator, exploded. Emerson Reynolds, the first to produce thiocarbamide and its nitrate (*loc. cit.*), records the tendency of the latter to decompose spontaneously, or even to explode.

Thiocarbamide and Oxalic Acid.

By reason of the sparing solubility of both substances in cold water, it could be foreseen that hydrolysis would defeat the isolation of any but a nearly insoluble salt; and when cold, saturated solutions were mixed and evaporated, this proved to be the case. A mixture of oxalic acid and thiocarbamide, in molecular proportions, was dissolved in the minimum amount of hot water; from this also, on cooling, a mixture of the components was deposited.

No better result was obtained by evaporating a cold solution in acetone. But when molecular proportions of thiocarbamide and of crystallised oxalic acid were together dissolved in about the minimum quantity of boiling acetone, a solid separated on cooling; when recrystallised from acetone, nearly saturated, in the cold, with oxalic acid, it formed small, white prisms melting at 73—74° and consisting of the anhydrous oxalate.

Found: $H_2C_2O_4 = 54\cdot2$.

$CH_4N_2S,H_2C_2O_4$ requires $H_2C_2O_4 = 54\cdot21$ per cent.

Acetic acid behaving for all practical purposes as a simple solvent of thiocarbamide, the idea occurred of using the former as a vehicle in which to present another acid for combination. On experiment, it proved that some salts are producible in this way; for example, when crystallised oxalic acid and thiocarbamide were together dissolved in the hot acid, the solution, as it cooled, deposited rosettes of nearly white, opaque prisms which were recrystallised from dry acetone. (Found, $H_2C_2O_4 = 54\cdot27$ per cent.)

Thiocarbamide and Trichloroacetic Acid.

A mixture of the constituents, in molecular proportion, was dissolved in about half its own weight of hot water, the solution, when cool, remaining clear. Chloroform was then added, to incipient

turbidity, and the turbidity dispelled by gentle warmth; on cooling, long, woolly-looking needles began to separate, changing, when the mixture was stirred, to short, white prisms, which were thoroughly washed with chloroform. The yield amounted to 64 per cent. of the theoretical, and the mother liquor gave a further crop. The salt was analysed by titration with alkali.

Found: $C_2HO_2Cl_3 = 68\cdot6$.
$CH_4N_2S,C_2HO_2Cl_3$ requires $C_2HO_2Cl_3 = 68\cdot3$ per cent.

In aqueous solution, the compound gave the reactions of thiocarbamide; with lead acetate, it yielded no precipitate, and hence was not a hydrochloride.

Thiocarbamide and Monochloroacetic Acid.

Attempts to obtain a salt of these, by the use of glacial acetic acid, first at the boiling point and next at 60°, were unsuccessful, the respective products being *iso*thiohydantoin hydrochloride and the hydrochloride of *iso*thiohydantoic acid (the latter is isomeric with thiocarbamide monochloroacetate). Rây and Fernandes's observation (T., 1914, **105**, 2160) was confirmed, that *iso*thiohydantoic acid hydrochloride is produced when a mixture of monochloroacetic acid and thiocarbamide, in acetone solution, is kept for twenty-four hours at the ordinary temperature.

Thiocarbamide and Picric Acid.

When to a hot concentrated solution of picric acid in glacial acetic acid 1 molecular proportion of thiocarbamide was added, the latter dissolved, communicating to the solution a deep orange colour. On cooling, long prisms separated, resembling monoclinic sulphur in colour and in appearance; by dissolution in water, or even in hot acetone, the compound was resolved into its components.

Found: $S = 10\cdot7$.
$CH_4N_2S,C_6H_3O_7N_3$ requires $S = 10\cdot5$ per cent.

On heating, the picrate first became dark brownish-red, and then melted, without deflagration.

Attempts to combine thiocarbamide, in the presence of water, with chloric, perchloric, silicofluoric, orthophosphoric, or metaphosphoric acid led to no decisive results; nor could a salt be obtained of phthalic, salicylic, tartaric, or dichloroacetic acid. In the last-named case an old observation (Dixon, T., 1893, **63**, 816) was confirmed, namely, that thiocarbamide, with dichloroacetic acid, yields

*iso*thiohydantoin hydrochloride—it is a curious reaction, and seems to merit further study.

Regarding the configuration of the additive compounds, produced from free acids, HX, and thiocarbamide, it is more than difficult to arrive at any precise judgment. In practically all cases where a compound, RX, unites additively with thiocarbamide, and the position of the more electropositive fraction, R, can be ascertained, the latter proves to be conjoined with the sulphur atom. Since this applies both to alkyl haloids and to acyl haloids, it may reasonably be supposed to hold also for hydrogen haloids and for free acids generally; in other words, the salt probably contains the SH-complex. Moreover, on the dissolution of thiocarbamide in acids, hydrogen sulphide is commonly disengaged, this phenomenon occurring not alone with the strong mineral acids, but also with feeble organic acids.

As to what becomes of the other radicle, X, we have at present no real knowledge. If it, too, combines with the sulphur, the product is a kind of sulphonium salt, $\begin{smallmatrix} NH_2 \\ NH_2 \end{smallmatrix}>C:S<\begin{smallmatrix} H \\ X \end{smallmatrix}$ (i); if it goes to the carbon atom, the result is $(NH_2)_2CX \cdot SH$ (ii); if somehow, in the long run, to the nitrogen atom, an ammonium salt must be formed, that is, $XNH_3 \cdot C(:NH) \cdot SH$ (iii), or a tautomeride. Form (ii), one may judge, is rather possible than probable; but, between (i) and (iii), so far as the author is aware, there are no facts yet known on which a decision may safely rest.

With a view to learn if (iii) is warrantable, the idea occurred of trying whether thiocarbamide thiocyanate (presumably

$$CSN_2H_4, HSCN)$$
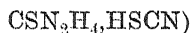
would undergo by heat the isomeric rearrangement, characteristic of primary ammonium thiocyanates, thus:

$$HS \cdot C(:NH) \cdot NH_3 \cdot SCN \longrightarrow HS \cdot C(:NH) \cdot NH \cdot CS \cdot NH_2.$$
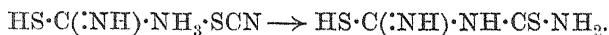
Here, a positive result would be decisive in favour of (iii). The accomplishment of the experiment has been defeated by an unforeseen impediment; in no way tried could the salt be prepared. Anhydrous thiocyanic acid was not employed, but, as an approximation, a hot, nearly saturated solution of barium thiocyanate in water (in which the salt is exceedingly soluble) was treated with one equivalent of thiocarbamide sulphate. From the filtered liquor nothing separated on cooling or on the addition of acetone; on spontaneous evaporation, thiocyanic acid escaped, the crystalline residue consisting merely of impure thiocarbamide. These failures were unexpected, because, from the properties of its salts,

one might suppose thiocyanic acid to resemble the strongest of the mineral acids.

Krall, also, has recorded (T., 1913, **103**, 1383) the failure of all attempts to produce thiocarbamide thiocyanate; as he gives no indication of the methods employed, it is uncertain how far these were alike or different in the two cases of independent endeavour.

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LXI.—*Catalysis.**   *Part III.   Some Induced Reactions.*

By NILRATAN DHAR.

WHEN an aqueous solution of mercuric chloride is boiled with oxalic acid, there is no reduction of the mercuric chloride to the mercurous state; but, as is well known, this mixture of mercuric chloride and oxalic acid decomposes at the ordinary temperature in sunlight according to the equation:

$$2HgCl_2 + H_2C_2O_4 = 2HgCl + 2HCl + 2CO_2.$$
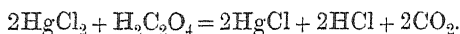
The same change, however, takes place in the dark, as the author has observed, if a drop of a $N/10$-solution of potassium permanganate is first added to the mixture; as soon as the colour of the permanganate is discharged, mercurous chloride begins to separate out.

This phenomenon appears to be of general occurrence. Thus the reduction of mercuric chloride and bromide by oxalic acid, tartaric acid, citric acid, malonic acid, malic acid, glycollic acid, lactic acid, hydroxylamine hydrochloride, hydrazine hydrochloride, etc., the reduction of gold chloride by several reducing agents, the reduction of silver nitrate, cupric chloride, and selenious acid (to selenium) by various organic acids, etc., are promoted by the addition of such oxidising agents as potassium permanganate, potassium persulphate, manganese dioxide, potassium nitrite, hydrogen peroxide, etc.

The experimental study of these induced reactions, as described below, shows that the effect is most marked in those cases which are sensitive to light.

* For Parts I and II, see *Proc. K. Akad. Wetensch., Amsterdam*, 1916, **18**, 1084, 1097.

Experimental.

In the majority of instances the materials used had been obtained from Kahlbaum, and in many cases they were recrystallised.

Measured volumes of the solutions were mixed and made up in every case to 100 c.c.; the mixtures then transferred to small Erlenmeyer flasks, and these were placed in a thermostat at a constant temperature. When sufficient time, as established by preliminary experiments, had been allowed for the completion of the reaction, the mercurous chloride formed was collected in a Gooch crucible and washed. The crucible was then heated at 105° in an air-oven until a constant weight was obtained.

According to the customary nomenclature (Luther and Schilow, *Zeitsch. physikal. Chem.*, 1903, **46**, 777), the substance which induces the chemical change is known as the "inductor" (for example, potassium permanganate), the substance which takes part in both the changes is called the "actor" (for example, oxalic acid), and the third substance is the "acceptor" (for example, mercuric chloride).

A. *Oxalic Acid and Mercuric Chloride with Various Oxidising Agents as Inductors.*

(1) *Inductor–Potassium Persulphate.*—Oxalic acid is slowly oxidised by potassium persulphate according to the equation:

$$K_2S_2O_8 + H_2C_2O_4 = 2CO_2 + 2KHSO_4.$$
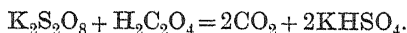
The mixtures, to which varying quantities of potassium persulphate were added, contained in each case 25 c.c. of $N/10$-oxalic acid and 20 c.c. of $N/10$-mercuric chloride, and the experiments were carried out at 100°:

0·0104 gram	$K_2S_2O_8$	gave	0·0248	gram	HgCl.
0·0235	,, $K_2S_2O_8$	,,	0·0555	,,	HgCl.
0·0306	,, $K_2S_2O_8$	,,	0·0674	,,	HgCl.
0·0585	,, $K_2S_2O_8$	,,	0·1937	,,	HgCl.
0·0694	,, $K_2S_2O_8$	,,	0·2007	,,	HgCl.
0·0912	,, $K_2S_2O_8$	,,	0·2076	,,	HgCl.
0·1303	,, $K_2S_2O_8$	,,	0·2080	,,	HgCl.
0·1884	,, $K_2S_2O_8$	,,	0·2266	,,	HgCl.
0·2381	,, $K_2S_2O_8$	,,	0·1888	,,	HgCl.
0·3303	,, $K_2S_2O_8$	,,	0·1464	,,	HgCl.
0·4208	,, $K_2S_2O_8$	,,	0·1143	,,	HgCl.
0·5539	,, $K_2S_2O_8$	,,	0·0720	,,	HgCl.
0·6549	,, $K_2S_2O_8$	,,	0·0280	,,	HgCl.

As shown by the figures in the foregoing table, the amount of mercurous chloride formed increases to a maximum and then falls off with the increase in the persulphate concentration.

Oxalates may be used instead of oxalic acid. Ammonium oxalate and mercuric chloride, when boiled, give a slight precipitate of mercurous chloride, but if a small crystal of potassium persulphate is first added, a copious precipitate is obtained.

(2) *Inductor—Manganese Dioxide.*—The manganese dioxide used in these experiments was obtained by allowing potassium permanganate to act on manganese sulphate in the presence of an excess of potassium or sodium nitrate; the precipitate produced consists of pure hydrated manganese dioxide. A weighed amount of this substance when air-dried was heated with a known volume of standard oxalic acid, containing sulphuric acid. A part of the oxalic acid was oxidised by manganese dioxide, whilst the excess was titrated with standard permanganate. In this way, the amount of hydration was determined, and in the following tables the calculated amounts of the anhydrous substance are given.

Each mixture contained 50 c.c. of $N/10$-oxalic acid and 20 c.c. of $N/10$-mercuric chloride:

	MnO_2 added.	HgCl produced.
	Gram.	Gram.
at 25°	0·0108	0·0975
	0·0225	0·1174
	0·0269	0·1285
at 100°	0·0114	0·1546
	0·0145	0·1785
	0·0234	0·1842

The effect of sulphuric acid on the reaction was studied by adding to the mixture 20 c.c. of $N/5$-sulphuric acid before making up to 100 c.c.:

	MnO_2 added.	HgCl produced.
	Gram.	Gram.
at 25°	0·0125	0·0712
	0·0214	0·0828
	0·0267	0·0875
at 100°	0·0110	0·1437
	0·0136	0·1612
	0·0224	0·1695

(3) *Inductor—Potassium Nitrite.*—The solid potassium nitrite prepared by the double decomposition of recrystallised silver nitrite and potassium chloride (compare Rây and Dhar, T., 1912, **101**, 965) was purified by recrystallisation from water. A solution was prepared and standardised by evaporating a known volume in a

platinum crucible on a steam-bath, heating the residue with sulphuric acid, and weighing the potassium sulphate formed.

Each mixture contained 25 c.c. of $N/10$-oxalic acid and 20 c.c. of $N/10$-mercuric chloride, and the experiments were carried out at 100°:

0·0091 gram KNO_2 gave 0·0590 gram HgCl.
0·0181   ,, KNO_2 ,,   0·0880   ,,   HgCl.
0·0272   ,, KNO_2 ,,   0·1171   ,,   HgCl.
0·0725   ,, KNO_2 ,,   0·1858   ,,   HgCl.
0·0907   ,, KNO_2 ,,   0·1984   ,,   HgCl.
0·1814   ,, KNO_2 ,,   0·2071   ,,   HgCl.
0·4535   ,, KNO_2 ,,   0·2214   ,,   HgCl.

The amount of mercurous chloride formed increases with the increase in the concentration of potassium nitrite.

When a small quantity of manganese sulphate is also present, the amount of mercurous chloride produced is independent of the concentration of potassium nitrite, and almost the whole of the mercuric salt is reduced, as the following table will show:

In the presence of 0·0654 gram $MnSO_4$:

0·0091 gram KNO_2 gave 0·2276 gram HgCl.
0·0453   ,, KNO_2 ,,   0·2274   ,,   HgCl.
0·0907   ,, KNO_2 ,,   0·2276   ,,   HgCl.
    (20 c.c. of $N/10$-mercuric chloride $= 0·2365$ gram HgCl.)

(4) *Inductor–Potassium Permanganate.*—The mixtures to which varying quantities of potassium permanganate were added contained in each case 50 c.c. of $N/10$-oxalic acid and 20 c.c. of $N/10$-mercuric chloride and the experiments were carried out at 25°:

C.c. of $N/10$-$KMnO_4$ added.	HgCl produced. Gram.
1	0·0663
2	0·0827
3	0·1063
5	0·1122
10	0·1224
20	0·1660

As shown by the figures in the foregoing table, the amount of mercurous chloride formed increases with the concentration of potassium permanganate. If the concentration of permanganate is kept constant, the amount of mercurous chloride obtained increases with the increase in the concentration of either the actor or acceptor, as shown by the figures in the following tables:

50 c.c. $N/10$-oxalic acid, 20 c.c. $N/10$-KMnO$_4$, and

30 ,, $N/10$-HgCl$_2$ gave 0·2026 gram HgCl at 25°.

20 ,, $N/10$-HgCl$_2$,, 0·1660 ,, HgCl ,,

10 ,, $N/10$-HgCl$_2$,, 0·1179 ,, HgCl ,,

35 c.c. $N/10$-oxalic acid, 20 c.c. $N/10$-KMnO$_4$, and

30 ,, $N/10$-HgCl$_2$ gave 0·1412 gram HgCl at 25°.

20 ,, $N/10$-HgCl$_2$,, 0·1248 ,, HgCl ,,

10 ,, $N/10$-HgCl$_2$,, 0·0875 ,, HgCl ,,

The effect of manganese salt on the reaction was studied by adding 0·0654 gram of manganese sulphate to the mixture of 50 c.c. of $N/10$-oxalic acid and 20 c.c. of $N/10$-mercuric chloride :

C.c. of $N/10$-KMnO$_4$ added.	HgCl. produced. Gram.
at 25° { 2	0·1420
5	0·1480
10	0·1551

The effect of sulphuric acid was studied by adding 4 c.c. of $N/2$-sulphuric acid to the same mixture :

C.c. of $N/10$-KMnO$_4$ added.	HgCl produced Gram.
1	0·0076
2	0·0616
3	0·0830
5	0·0893
10	0·1067
20	0·1206

It will be evident from the foregoing tables that manganese sulphate promotes, whilst sulphuric acid hinders the reduction. The joint effect of manganese sulphate and sulphuric acid was studied by adding 10 c.c. of N-sulphuric acid in one case and 10 c.c. of N-sulphuric acid and 0·0654 gram of manganese sulphate in the other, to the mixture of 25 c.c. of $N/10$-oxalic acid and 10 c.c. of $N/10$-mercuric chloride :

C.c. KMnO$_4$ added.	HgCl obtained with no manganese salt. Gram.	HgCl obtained with 0·0654 gram. MnSO$_4$. Gram.
at { 5	0·0348	0·0556
100° { 10	0·0425	0·0554
20	0·0184	0·0194

Hence, even in the presence of sulphuric acid, manganese sulphate promotes the reaction.

(5) *Inductor—Chromic Acid.*—Chromic acid when added to a mixture of mercuric chloride and oxalic acid, does not give a precipitate of mercurous chloride. In a subsequent paper it will be shown that the velocity of the oxidation of oxalic acid by chromic acid is

low. This oxidation, however, is greatly accelerated by manganese salts, and accordingly, if chromic acid and manganese sulphate together are added to the mixture of mercuric chloride and oxalic acid, a precipitate of mercurous chloride is obtained.

Ordinary pure chromic acid was several times washed with concentrated nitric acid, then dissolved in the minimum quantity of water, and reprecipitated by the addition of concentrated nitric acid. This product was heated in a steam-bath in order to free it from nitric acid, and finally purified by crystallisation from water.

The mixtures to which varying quantities of manganese sulphate were added contained in each case 25 c.c. of $N/10$-oxalic acid, 20 c.c. of $N/10$-mercuric chloride, and 0·00253 gram of chromic acid:

MnSO$_4$ added. Gram.	HgCl produced at 25°. Gram.	HgCl produced at 100°. Gram.
0·00327	0·0107	0·0259
0·00654	0·0306	0·1351
0·01308	0·0850	0·1685
0·01962	0·0887	0·1721
0·03924	0·1042	0·2039
0·05886	0·1074	0·2142
0·1308	0·1121	0·2232
0·1962	0·1120	0·2238

As shown by the figures in the foregoing table, the amount of mercurous chloride formed increases with the concentration of manganese sulphate. To the same mixture of mercuric chloride and oxalic acid, 0·01962 gram of manganese sulphate and varying quantities of chromic acid were added:

	Chromic acid added. Gram.	HgCl obtained. Gram.
	0·00253	0·0887
at	0·00606	0·1075
25°	0·01515	0·0776
	0·02525	0·0462

Hence, with a definite concentration of manganese salt, the amount of mercurous chloride formed increases to a maximum and then decreases with the increase in the concentration of chromic acid.

The effect of sulphuric acid was studied by adding 10 c.c. of N-sulphuric acid to the mixture containing 40 c.c. of $N/10$-oxalic acid, 20 c.c. of $N/10$-mercuric chloride, and 0·0654 gram of manganese sulphate with varying quantities of chromic acid:

Chromic acid added. Gram.	HgCl obtained with no H$_2$SO$_4$. Gram.	HgCl produced with 10 c.c. H$_2$SO$_4$. Gram.
0·00101	0·1052	0·0474
0·00253	0·1162	0·0503
0·00656	0·1254	0·0518

Hence sulphuric acid is a retarder.

(6) *Inductor—Nitric Acid.*—Nitric acid by itself cannot produce a precipitate of mercurous chloride when it is added to a mixture of mercuric chloride and oxalic acid; but nitric acid with manganese sulphate produces the precipitate. The oxidation of oxalic acid by nitric acid is also accelerated by manganese salts. Varying amounts of nitric acid were added to the mixture containing 40 c.c. of $N/10$-oxalic acid, 20 c.c. of $N/10$-mercuric chloride, and 0·1962 gram of manganese sulphate, and the following results were obtained at 100°:

C.c. N-HNO$_3$. added.	HgCl obtained. Gram.
0·1	0·2055
0·2	0·2052
0·5	0·2058

In the presence of manganese sulphate, the amount of mercurous chloride produced is independent of the concentration of nitric acid.

The following is a summary of the results obtained with oxalic acid as actor:

(*a*) The greater the concentration of the inductor the greater is the amount of mercurous chloride obtained; this relation holds up to a certain limiting concentration of the inductor, after which an increase in the concentration of the inductor is accompanied in most cases by a decrease in the amount of mercurous chloride.

(*b*) The higher the temperature the greater is the amount of mercurous chloride formed.

(*c*) The greater the concentration of the actor (that is, oxalic acid), the greater is the amount of reduction.

(*d*) Sulphuric acid hinders and manganese sulphate promotes the reaction.

B. *Tartaric Acid and Mercuric Chloride with various Oxidising Agents.*

As in the experiments already described, the total volume of the reaction mixture was 100 c.c. All the experiments recorded below were carried out at 100°, except where otherwise indicated:

C.c. tartaric acid used.	C.c. $N/10$-HgCl. used.	Vol. oxidising agent added.	HgCl obtained. Gram.
50 of $N/5$	25	10 c.c. $N/10$-KMnO$_4$	0·0557
50 ,, $N/5$	25	20 ,, $N/10$-KMnO$_4$	0·1133
50 ,, $N/5$	25	5 ,, $N/10$-K$_2$S$_2$O$_8$	0·0143
50 ,, $N/5$	25	10 ,, $N/10$-K$_2$S$_2$O$_8$	0·0295
50 ,, $N/5$	25	20 ,, $N/10$-K$_2$S$_2$O$_8$	0·0613
50 ,, $N/5$	10	5 ,, $N/5$-H$_2$O$_2$	0·0247
50 ,, $N/5$	10	10 ,, $N/5$-H$_2$O$_2$	0·0478
25 ,, $N/10$	25	3 ,, $N/10$-KMnO$_4$	0·0177
25 ,, $N/10$	25	10 ,, $N/10$-KMnO$_4$	[0·0024 gram at 25°] 0·0457

From the foregoing results it appears that the greater the concentration of the inductor, that is, the added oxidising agent, the greater is the amount of mercurous chloride formed. With a definite concentration of the inductor the amount of mercurous chloride formed increases (*a*) with the concentration of the actor (tartaric acid), and (*b*) with the temperature.

C. *Malic Acid and Mercuric Chloride with Oxidising Agents as Inductors.*

In each experiment 30 c.c. of $N/10$-malic acid and 10 c.c. of $N/10$-mercuric chloride were used, the quantity of inductor given in the following table was added, and the volume made up to 100 c.c. Except where otherwise indicated, the experiments were carried out at 100°:

5 c.c. $N/10$-KMnO$_4$ gave 0·0297 gram HgCl (0·0070 gram at 25°).

3 c.c. gave 0·0189 gram HgCl (0·0035 gram at 25°).

5 c.c. $N/10$-K$_2$S$_2$O$_8$ gave 0·0153 gram HgCl and 3 c.c. gave 0·0110 gram.

5 c.c. $N/5$-H$_2$O$_2$ gave 0·0112 gram HgCl and 3 c.c. gave 0·0074 gram.

D. *Malonic Acid and Mercuric Chloride with Oxidising Agents as Inductors.*

Twenty-five c.c. of $N/10$-malonic acid and 10 c.c. of $N/10$-mercuric chloride were used for each experiment at 100°:

5 c.c. $N/10$-KMnO$_4$ gave 0·0201 gram HgCl and 3 c.c. gave 0·0118 gram.

5 c.c. $N/5$-H$_2$O$_2$ gave 0·0159 gram HgCl and 3 c.c. gave 0·0107 gram.

E. *Glycollic Acid and Mercuric Chloride with Oxidising Agents as Inductors.*

Twenty-five c.c. of $N/10$-glycollic acid and 15 c.c. of $N/10$-mercuric chloride were used in each experiment at 100°:

5 c.c. $N/10$-KMnO$_4$ gave 0·0113 gram HgCl and 3 c.c. gave 0·0077 gram.

5 c.c. $N/10$-K$_2$S$_2$O$_8$ gave 0·0054 gram HgCl and 3 c.c. gave 0·0031 gram.

10 c.c. $N/5$-H$_2$O$_2$ gave 0·0107 gram HgCl and 5 c.c. gave 0·0069 gram.

F. *Citric Acid and Mercuric Chloride with Oxidising Agents as Inductors.*

In each experiment at 100°, 10 c.c. of $N/10$-mercuric chloride were used:

Volume of citric acid used.	Volume of oxidising agent added.	HgCl obtained. Gram.
10 c.c. of N-acid	5 c.c. of $N/5$-H_2O_2	0·0026
10 ,, N-acid	3 ,, $N/5$-H_2O_2	0·0017
25 ,, $N/10$-acid	5 ,, $N/10$-KMnO$_4$	0·0167
25 ,, $N/10$-acid	3 ,, $N/10$-KMnO$_4$	0·0099

G. *Hydrazine Hydrochloride and Mercuric Chloride with Potassium Permanganate as Inductor*

In each experiment 20 c.c. of N-hydrazine hydrochloride and 10 c.c. of $N/10$-mercuric chloride were used and measurements were made at 100°:

10 c.c. N-KMnO$_4$ gave 0·0314 gram HgCl and 5 c.c. gave 0·0212 gram.

H. *Hydroxylamine Hydrochloride and Mercuric Chloride with Potassium Permanganate as Inductor.*

In each experiment at 100°, 15 c.c. of N-hydroxylamine hydrochloride and 10 c.c. of $N/10$-mercuric chloride were used:

10 c.c. N-KMnO$_4$ gave 0·0236 gram HgCl and 5 c.c. gave 0·0114 gram.

From the experiments recorded in B to H it appears, as from the experiments in A, that the greater the concentration of the inductor the greater is the amount of mercurous chloride formed.

The activity of hydrogen peroxide as an oxidising agent in these cases, especially with tartaric and citric acids, is greatly increased by either ferric or ferrous salt. Thus, if mercuric chloride is boiled with tartaric acid and hydrogen peroxide is added to the mixture, a small amount of mercurous chloride is obtained, but if a drop of a ferric or ferrous salt is added to the mixture, an immediate, copious precipitate of mercurous chloride is formed. In Fenton's reagent, ferrous salt is used, but in these cases both ferrous and ferric salts are equally active.

Experiments were made with mercuric bromide instead of mercuric chloride, and results similar to those with mercuric chloride were obtained with all the reducing agents.

J. *Copper Chloride and Organic Acids with Potassium Permanganate as Inductor.*

When copper chloride is boiled with tartaric acid, for example, no reduction to the cuprous state takes place, but when potassium permanganate is added to the mixture, then reduction occurs. In these cases, no precipitate of cuprous salt was obtained, but the cuprous salt formed remained in solution as part of a complex negative ion.

To this solution potassium iodide was added, and the liberated iodine was estimated with standard thiosulphate. In this way, only the copper in the cupric state can be determined. The original cupric chloride solution having been treated in the same manner, the difference gave the amount of cuprous salt formed.

In each experiment 0·2194 gram of cupric chloride was used and the volume of the reaction mixture made up to 100 c.c., measurements being made at 100°:

Volume of acid used.	Volume of $N/10$-KMnO$_4$ added.	Cuprous salt produced. Gram.	Percentage reduction.
25 c.c. of $N/2$-tartaric	40 c.c.	0·0538	25
25 ,, ,,	20 ,,	0·0266	12
25 ,, N-citric	40 ,,	0·0202	9
25 ,, ,,	25 ,,	0·0124	5·5
35 ,, $N/2$-lactic	40 ,,	0·0154	7
35 ,, ,,	25 ,,	0·0101	4·5
25 ,, $N/5$-malic	40 ,,	0·0112	5
25 ,, ,,	25 ,,	0·0065	3

The foregoing figures show that potassium permanganate promotes the reduction of cupric chloride by tartaric acid, citric acid, etc.

Oxalic acid cannot be used as a reducing agent, since cupric oxalate immediately separates out when the acid is added to the cupric salt.

K. *Gold Chloride and Organic Acids with Various Inductors.*

Gold chloride is reduced more rapidly by reducing agents when an oxidising agent is added to the mixture. When the reduction is effected by hydrogen peroxide and a few drops of potassium permanganate are added, the colour of the latter is discharged in a few seconds, and almost immediately black particles of gold, gradually becoming brown, separate out. This may serve as a lecture experiment on induced reactions; instead of hydrogen peroxide, a solution of percarbonate may be used with similar effect.

The gold chloride used in the following experiments contained 1·8 grams of gold per litre. The volume of the reaction mixture in each case was 25 c.c., and the experiments were made at 25°:

Volume of gold chloride used.	Volume of reducing agent used.	Volume of oxidising agent added.	Time required for appearance of gold particles.
2 c.c.	5 c.c. $N/10$-oxalic acid	0	10′ 0″
2 ,,	5 c.c. $N/10$-oxalic acid	0·1 c.c. $N/10$ KMnO$_4$	4′ 0″
2 ,,	5 c.c. $N/10$ oxalic acid	0·2 c.c. $N/10$-KMnO$_4$	2′ 20″
5 ,,	5 c.c. $N/10$-tartaric acid	0	40′ 30″
5 ,,	5 c.c. $N/10$-tartaric acid	0·3 c.c. $N/10$-KMnO$_4$	10′ 0″
5 ,,	5 c.c. $N/10$-tartaric acid	0·5 c.c. $N/10$-KMnO$_4$	7′ 2″
5 ,,	5 c.c. $N/10$-citric acid	0	26′ 6″
5 ,,	5 c.c. $N/10$-citric acid	0·5 c.c. $N/10$-KMnO$_4$	7′ 5″
5 ,,	5 c.c. $N/10$-citric acid	0·75 c.c. $N/10$-KMnO$_4$	5′ 20″
5 ,,	5 c.c. $N/10$-malic acid	0	46′ 0″
5 ,,	5 c.c. $N/10$-malic acid	0·5 c.c. $N/10$-KMnO$_4$	12′ 0″
5 ,,	5 c.c. $N/10$-malonic acid	0	20′ 10″
5 ,,	5 c.c. $N/10$-malonic acid	0·5 c.c. $N/10$-KMnO$_4$	5′ 5″
5 ,,	10 c.c. $N/5$-H$_2$O$_2$	0	9′ 40″
5 ,,	10 c.c. $N/5$-H$_2$O$_2$	0·5 c.c. $N/10$-KMnO$_4$	2′ 5″
5 ,,	10 c.c. $N/100$-H$_2$SO$_3$	0	5′ 30″
5 ,,	10 c.c. $N/100$-H$_2$SO$_3$	0·5 c.c. $N/10$-K$_2$S$_2$O$_8$	0′ 20″
2 ,,	5 c.c. $N/100$-H$_2$SO$_3$	0	5′ 40″
2 ,,	5 c.c. $N/100$-H$_2$SO$_3$	0·1 c.c. $N/10$-KMnO$_4$	0′ 40″
2 ,,	5 c.c. $N/100$-H$_2$SO$_3$	0·2 c.c. $N/10$-KMnO$_4$	0′ 30″

L. *Silver Nitrate and Organic Acids with Potassium Permanganate as Inductor.*

When a solution of silver nitrate is boiled with tartaric acid, citric acid, etc., there is practically no reduction, but when potassium permanganate is added to the mixture, black silver particles separate out. The volume of the reaction mixture was made up to 25 c.c. and measurements were made at 60°. In each experiment 5 c.c. of $N/10$-silver nitrate were used:

Volume of reducing agent used.	Volume of $N/10$-KMnO$_4$ added.	Time required for the appearance of silver.
10 c.c. $N/5$-malic acid	3 c.c.	6′
10 c.c. $N/5$-malic acid	1 ,,	15′
10 c.c. $N/5$-tartaric acid	3 ,,	5′
10 c.c. $N/5$-tartaric acid	1 ,,	13′
10 c.c. $N/4$-citric acid	4 ,,	5′
10 c.c. $N/4$-citric acid	1·5 ,,	20′
10 c.c. $N/10$-malonic acid	3 ,,	12′
10 c.c. $N/10$-malonic acid	1 ,,	30′
10 c.c. $N/10$-lactic acid	3 ,,	16′
10 c.c. $N/10$-lactic acid	1 ,,	46′

M. *Sodium Selenite and Reducing Agents with Potassium Permanganate as Inductor.*

Sodium selenite is not reduced to selenium at the ordinary temperature by oxalic acid, tartaric acid, etc.; reduction takes place only when potassium permanganate is added to the mixture. Measurements were made with 10 c.c. of $N/5$-sodium selenite at 25°, the volume of the reactor mixture being 25 c.c.:

Volume of reducing agent used.	Volume of $N/10$-KMnO$_4$ added.	Time for the appearance of Se.
10 c.c. $N/10$-oxalic acid	3 c.c.	8′ 10″
10 c.c. $N/10$-oxalic acid	2 ,,	12′ 5″
10 c.c. $N/5$-tartaric acid	3 ,,	12′ 50″
10 c.c. $N/5$-tartaric acid	2 ,,	19′ 10″
10 c.c. $N/4$-citric acid	3 ,,	10′ 5″
10 c.c. $N/4$-citric acid	2 ,,	17′ 0″
10 c.c. $N/10$-malonic acid	3 ,,	15′ 22″
10 c.c. $N/10$-malonic acid	2 ,,	22′ 30″
10 c.c. $N/5$-malic acid	3 ,,	13′ 10″
10 c.c. $N/5$-malic acid	2 ,,	20′ 5″
10 c.c. N-hydroxylamine hydrochloride	3 ,,	3′ 10″
10 c.c. N-hydroxylamine hydrochloride	2 ,,	5′ 2″
10 c.c. N-hydrazine hydrochloride	3 ,,	5′ 7″
10 c.c. N-hydrazine hydrochloride	2 ,,	8′ 30″

From the experiments recorded in the foregoing tables, it appears that the greater the concentration of the inductor, potassium permanganate, the more rapid is the reduction.

Change of Conductivity in Induced Reactions.

With the object of obtaining further information on the course of these induced reactions, measurements of electric conductivity were undertaken.

Fresh solutions of all the reacting substances in "conductivity water" were prepared and measurements carried out by the usual Kohlrausch method. Experiments were made with oxalic and malonic acids as actors, mercuric and gold chlorides as acceptors, and potassium permanganate as inductor. The conductivity of the reaction mixture falls off very rapidly at first, and as soon as the reduction of the metallic salt begins, the conductivity again rises slowly. The following table will illustrate a typical change of conductivity. Fifty c.c. of $N/10$-oxalic acid, 20 c.c. of $N/10$-mercuric chloride, and 20 c.c. of $N/10$-potassium permanganate were mixed :

Time.	Specific conductivity at 25°.
0	0·00823
5′	0·00726
10′	0·00588
15′	0·00392
20′	0·00309
25′	0·00315
30′	0·00334
35′	0·00341
40′	0·00345
45′	0·00348
50′	0·00352
55′	0·00358
60′	0·00364
65′	0·00365

If the reacting organic acid were first converted into formic acid, the fall in conductivity would almost certainly not have been so very rapid, and the conductivity measurements do not support the view of the intermediate formation of formic acid as a product of the oxidation of oxalic or malonic acid. The rapid fall of conductivity is most probably due to the oxidation of the organic acid (for example, oxalic, malonic, etc.) straight away to the almost non-conducting carbon dioxide and water. The second slow increase is to be attributed to the formation of hydrochloric acid, which is a product of the change.

Attempts have been made to study the kinetics of these induced reactions, and from the experimental results curves showing definite period of induction are obtained. No definite conclusion as to the course of these reactions can, however, be obtained.

Mercuric chloride may be used as an indicator showing the acceleration of the oxidation of oxalic acid by any substance; when there is an acceleration, mercurous chloride is obtained. It seems probable that when there is acceleration of the oxidation of oxalic acid by a catalyst, a substance with greater reducing power than oxalic acid is formed; thus, when the indicator, mercuric chloride, is present in the oxidation of oxalic acid by chromic acid, mercurous chloride is not formed; on the other hand, if manganese sulphate is added to the mixture, there is a marked acceleration of the oxidation of oxalic acid by chromic acid, and simultaneously a precipitate of mercurous chloride is obtained.

In order to throw further light on these reactions, the kinetics of individual reactions involved in these complex changes have been separately investigated and are described in the following paper. The kinetic measurements will show that the order of the oxidation of oxalic acid by chromic acid in the presence of manganese salts is quite different from that of the reaction in which no manganese salt is present.

Moreover, it is seen that manganese is quite unique in its behaviour in this oxidation; cobalt or iron or chromium salts cannot be used instead of manganese salts.

Discussion of Results.

In all the experiments on induced reactions recorded above, the oxidising agents take part and are themselves reduced during the chemical change. According to Wagner (*Zeitsch. physikal. Chem.*, 1899, **28**, 33), these reactions may be regarded as examples of pseudo-catalysis. Ostwald uses the term " catalysis by transvec- tion " (Uebertragungskatalyse).

On consulting the literature on the subject, it is observed that practically no instance exactly of this nature is known. The work on induced reactions recorded hitherto refers to reactions with two reducing agents and one oxidising agent. In the reactions investigated in this paper there are two oxidising agents (for example, mercuric chloride and potassium permanganate) and only one reducing agent (for example, oxalic acid or sulphurous acid).

At first the primary change, namely, the oxidation of the reducing agent by the inductor (potassium permanganate or hydrogen peroxide), takes place, and this primary change induces or promotes the secondary change, that is, the reduction of the acceptor (for example, mercuric chloride) by the actor (for example, oxalic acid). In other words, the potential oxidising power of mercuric chloride is activated by the previous oxidation due to the inductor.

The reducing agent divides itself, as it were, between the two oxidising agents, and the proportion in which it is divided between the two oxidising agents may be termed the induction factor (I) (compare Luther and Schilow, *loc. cit.*):

$$I = \frac{\text{amount of acceptor transformed}}{\text{amount of inductor used up.}}$$

It can be shown theoretically that the induction factor would be proportional to the ratio of the concentrations of mercuric chloride and potassium permanganate at the beginning of the reaction. From the figures on p. 693, one finds that 50 c.c. of $N/10$-oxalic acid, 20 c.c. of $N/10$-mercuric chloride, and

1 c.c. $N/10$-KMnO$_4$ gave 0·0663 gram HgCl$\equiv$2·9 c.c. $N/10$-oxalic acid.

2 c.c. $N/10$-KMnO$_4$ gave 0·0827 gram HgCl$\equiv$3·5 c.c. $N/10$-oxalic acid.

3 c.c. $N/10$-KMnO$_4$ gave 0·1063 gram HgCl$\equiv$4·53 c.c. $N/10$-oxalic acid.

5 c.c. $N/10$-KMnO$_4$ gave 0·1122 gram HgCl$\equiv$4·95 c.c. $N/10$-oxalic acid.

10 c.c. $N/10$-KMnO$_4$ gave 0·1224 gram HgCl$\equiv$5·3 c.c. $N/10$-oxalic acid.

20 c.c. $N/10$-KMnO$_4$ gave 0·1660 gram HgCl$\equiv$7·0 c.c. $N/10$-oxalic acid.

Hence the induction factors are:

2·9/1,	3·50/2,	4·53/3,	4·95/5	5·3/10,	7/20
= 2·9	1·75	1·5	0·99	0·53	0·35

F F*

The maximum limit of the induction factor in this reaction is 3. Consequently it follows that the inductor (potassium permanganate) will receive and oxidise 1 molecule of oxalic acid, whilst the acceptor (mercuric chloride) will oxidise 3 molecules. On comparing these values of the induction factor (I) with the corresponding ratios of the concentrations of mercuric chloride (C_a) and potassium permanganate (C_i) at the beginning of the reaction, the following results are obtained:

$$I \quad = \quad 0.35 \quad 0.53 \quad 0.99 \quad 1.50 \quad 1.75 \quad 2.9$$
$$C_a/C_i = \quad 1 \quad\quad 2 \quad\quad 4 \quad\quad 6.66 \quad 10 \quad\quad 20$$

From the foregoing figures it appears that the induction factor increases as the ratio of the concentrations of mercuric chloride and potassium permanganate at the beginning of the reaction is increased.

In the phenomenon of co-fermentation we have a physiological analogue of these reactions. Magnus (*Zeitsch. physiol. Chem.*, 1904, **42**, 149) has shown that one enzyme is able to do its special work only in the presence of another enzyme. Further, Ipatiev's method for the hydrogenation of organic compounds (*Ber.*, 1907, **40**, 1270, 1281; 1909, **42**, 2089) furnishes another analogue of these reactions. In his method a variety of catalysts—alumina, nickel oxide, copper oxide, etc—is used, and in the presence of these catalysts reductions are effected by hydrogen. Here oxidising agents (for example, copper oxide, alumina, etc.) are used in helping a reduction. Ipatiev tentatively explains the process on the assumption that at first the metallic oxide is reduced with the formation of water, which regenerates the oxide and liberates active hydrogen.

The mechanism of these induced reactions is still obscure. Luther and Schilow's work (*loc. cit.*) does not take us further than their classification. By some investigators the formation of an intermediate compound is regarded as important in the mechanism of induced reactions, but Dixon (T., 1886, **49**, 94) has pointed out that the mere isolation of such a product does not necessarily prove that the reaction proceeds in that particular way. The assumed intermediate compound may be, in reality, a by-product of the reactions.

In order that a chemical change can occur at all, it must be associated with the diminution of free energy. This loss depends only on the initial and final stages of the reaction, not on its course. On the other hand, the velocity of the reaction is strictly proportional to this loss. Hence we should be inclined to conclude that the velocity of the reaction in a given system must have the same value, whether the process is direct or indirect—

whether it takes place in one or several steps. Such a conclusion would be incorrect, for, besides the loss of free energy, the velocity of reactions depends on many factors, which are by no means all known. Hence Ostwald has urged that the velocity of each separate reaction concerned must be actually measured. The application of this method to complex reactions yields evidence that in some cases at least intermediate compounds are formed. The study of the oxidation of oxalic acid by chromic acid with and without manganese sulphate (see following paper) has proved that although the final products·are the same in both cases, yet in the presence of the positive catalyst, manganese sulphate, the order of the reaction is altogether changed. Hence it seems reasonable to suppose that in the presence of manganese sulphate some kind of intermediate compound takes part in the change.

It has been suggested that in induced reactions hydrogen peroxide is first formed (compare Kastle and Loevenhart, *Amer. Chem. J.*, 1903, **29**, 397, 517); but the foregoing results have shown that hydrogen peroxide itself is a much less active inductor than potassium permanganate. Moreover, a solution of mercuric chloride when boiled with hydrogen peroxide gives scarcely any precipitate of mercurous chloride.

As regards the oxidation of organic acids, it is conceivable that formic acid is the first product. Pean de Saint Gilles (*Ann. Chim. phys.*, 1850) has shown that in sulphuric acid solution the oxidation of tartaric acid by potassium permanganate takes place according to the equation:

$$C_4H_6O_6 + 3O = 2H \cdot CO_2H + 2CO_2 + H_2O.$$
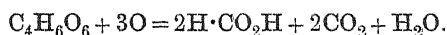
As a matter of fact, the formic acid produced can be distilled off and collected. In order to test whether there is any ground for assuming the intermediate production of formic acid in the oxidation of oxalic acid, the following experiments were made. The induction due to chromic acid and manganese sulphate was studied at 0°. The reacting substances were previously cooled to 0° before mixing, and the reaction was allowed to proceed at that temperature for twenty hours; the mercurous chloride formed was quickly collected in a Gooch crucible. The total volume of the mixture in each case was 100 c.c.

Twenty-five c.c. $N/10$-oxalic acid, 20 c.c. $N/10$-$HgCl_2$, and

Chromic acid. Gram.	HgCl produced [0·0654 gram $MnSO_4$] Gram.	HgCl produced [0·0327 gram $MnSO_4$]. Gram.
0·00101	0·0260	0·0185
0·00253	0·0379	0·0276
0·00505	0·0470	0·0284
0·01515	0·0326	0·0202

The experiments show clearly that even at 0° the induction takes place. On the other hand, when a mixture of 25 c.c. of $N/3$-formic acid and 20 c.c. of $N/10$-mercuric chloride was made up to 100 c.c. and kept at 0° for twenty hours, no precipitate of mercurous chloride was obtained; it was further observed that $N/10$-sodium formate cannot reduce mercuric chloride at 0°. Evidently these experiments prove that formic acid cannot be an intermediate product in the oxidation of oxalic acid.

The analogy between these induced reactions and photo-chemical reactions has already been referred to. D. Berthelot (*Compt. rend.*, 1910, **150**, 1327) stated that oxalic acid when exposed to light produced formic acid and carbon dioxide. The author has observed that if silver chloride or bromide or mercuric iodide is exposed to sunlight with a solution of an oxalate for a sufficient length of time, and the mixture is agitated, reduction takes place to metallic silver and mercurous salt respectively. On the other hand, reduction does not take place in any of these cases with formates or formic acid. Again, if an oxalate is added to a solution of a cupric salt, a precipitate of cupric oxalate is obtained, and if an excess of the oxalate is added, the precipitate dissolves to a blue solution. This complex copper oxalate solution is sensitive to light and decomposes on exposure to sunlight into metallic copper and carbon dioxide. On the other hand, the blue solution of a complex formate obtained by mixing excess of ammonium formate with a cupric salt can be boiled without any change; and it does not decompose when exposed to sunlight.

The facts just cited do not support the idea of the production of formates when oxalates and oxidising agents (for example, silver salts, copper salts, etc.) are exposed to light.

In the case of induced reactions, the analogy between the behaviour of an inductor and that of light is quite striking; the behaviour of a mixture of mercuric chloride and oxalic acid in the presence of potassium permanganate and of light is an illustration of the point. Not only is the mixture extremely sensitive to both these agents, but the shining crystals of mercurous chloride obtained in the two cases as the product of the reaction are closely similar in appearance. The analogy between photochemical reactions and those in which chemical catalysts play a part will be further developed in the following paper.

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LXII.—*Catalysis. Part IV. Temperature Coefficients of Catalysed Reactions.*

By Nilratan Dhar.

In the foregoing paper it has been shown that although oxalic acid cannot reduce mercuric chloride even when boiled, the addition of a few drops of chromic acid and a trace of manganese salt is followed by the reduction of the chromic acid, and immediately thereafter by the reduction of mercuric chloride. It is the object of the present communication to throw light on the mechanism of this and other induced reactions, and, further, to study the temperature coefficients of reactions influenced by chemical catalysts or by light. The effect of change in the concentration of the reacting substances on temperature coefficients has also been investigated.

The investigation has covered the kinetics of the oxidation of oxalic acid and formic acid by chromic acid, and the oxidation of formates and oxalates by iodine, mercuric chloride, and silver nitrate.

Experimental.

Oxalic Acid and Chromic Acid.

Oxalic acid is slowly oxidised by chromic acid at the ordinary temperature, but at about 25° the velocity of the reaction is quite measurable.

Ordinary pure chromic acid was repeatedly washed with concentrated nitric acid in order to remove potassium salts. The washed specimen was dissolved in the minimum quantity of water and precipitated with concentrated nitric acid; this product was freed from nitric acid by heating it electrically in a vacuum desiccator over potassium hydroxide. The product was finally purified by recrystallisation from "conductivity water" and dried in a steam oven.

The ordinary pure oxalic acid was first crystallised from water to which were added a few drops of hydrochloric acid in order to decompose any sodium oxalate if present. This product was several times recrystallised from water and dried centrifugally.

Measured volumes of oxalic acid and chromic acid which had been previously brought to a constant temperature in a thermostat were rapidly mixed, and the time was noted. After definite intervals of time, measured quantities were withdrawn by means of calibrated pipettes. The unchanged chromic acid remaining

was allowed to act on a mixture of potassium iodide and hydrochloric acid, and the iodine liberated was estimated with standard thiosulphate. The thiosulphate solution was prepared in distilled water freed from carbon dioxide and was about $N/60$.

The thermostat regulators used were spiral ones filled with toluene (Lowry type), and the Götze thermometers (divided into tenths) employed in the thermostats were checked against a normal thermometer which had been calibrated by the National Physical Laboratory.

Order of the Reaction.—The velocity of the reaction may be represented by an equation of the form $-dc_1/dt = kc_1^m c_2^n$, where c_1 and c_2 represent concentrations of chromic acid and oxalic acid respectively.

Determination of m.—In the following series of experiments the oxalic acid used was in large excess, and hence the concentration may be taken as practically constant during the course of the reaction; thus the velocity equation takes the following form: $-dc_1/dt = (kc_2^n)c_1^m = k_1 c_1^m$, where $k_1 = kc_2^n$. The order of the reaction under the conditions specified is therefore the same as m.

Since the free chromic acid in the solution is equivalent to the amount of thiosulphate required, it is sufficient to give for each observation the amount of thiosulphate in c.c. The results recorded in the following four Tables were all obtained at 25°.

TABLE I.

$N/5$-oxalic acid and $N/100$-chromic acid.

Time in minutes.	C.c. of Thiosulphate.	$k_1 = 1/t \log c_0/c$.
0	31·3	——
8	21·7	0·0198
17	14·45	0·0197
33	6·95	0·0198
43·5	4·25	0·0199
70·5	1·25	0·0198
	Mean	0·0198

TABLE II.

$3N/20$-oxalic acid and $N/100$-chromic acid.

0	31·3	——
20	20·5	0·00919
38	14·0	0·00919
50	10·9	0·00916
67	7·65	0·00913
89	4·9	0·00905

TABLE III.

$N/10$-oxalic acid and $N/100$-chromic acid.

Time in minutes.	C.c. of Thiosulphate.	$k_1 = 1/t \log c_0/c$.
0	31·25	—
23	25·6	0·00376
52	20·4	0·00356
91	15·2	0·00344
127	11·85	0·00332
167	9·1	0·00320

TABLE IV.

$N/20$-oxalic acid and $N/100$-chromic acid.

0	34·6	—
156	27·8	0·000602
197	26·45	0·000592
354	21·95	0·000558
610	15·5	0·000515
1250	10·25	0·000422

It appears that, in spite of a slight tendency to fall off, the values of k_1 calculated for $m = 1$ exhibit such a degree of constancy that the equation indicating a unimolecular reaction may fairly be regarded as the appropriate one. Hence, in the presence of a large excess of oxalic acid, the oxidation follows the unimolecular law.

Determination of n.—The method used was Ostwald's "isolation method." As remarked before, the constant k_1 involves the concentration of the oxalic acid in a manner expressed by the equation $k_1 = kc^n$, where k is the intrinsic velocity coefficient, c the concentration of oxalic acid, and n the number of oxalic acid molecules taking part in the reaction. Supposing that k_1' and k_1'' are the values of k_1 obtained in two experiments, in each of which the initial concentration of chromic acid is the same, whilst the concentrations of oxalic acid are different, say c'_2 and c''_2, the following equations are obtained:

$$k_1' = kc_2'^n, \quad k_1'' = kc_2''^n, \text{ whence } n = \log \frac{k_1'}{k_1''} \Big/ \log \frac{c_2'}{c_2''}.$$

In using the measurements recorded in the foregoing Tables for the purpose of determining n, those values of k_1 are chosen where the amounts of unchanged chromic acid are approximately equal in the separate series. On comparing the Tables, the following results are obtained:

Concentration of oxalic acid......	(1) $N/5$	(2) $3 N/20$	(3) $N/10$	(4) $N/20$
Value of k_1	0·0198	0·00916	0·00320	0·000422

It is evident that the values of k_1 decrease rapidly as the concentration of oxalic acid diminishes, which indicates a high value for the exponent n.   The actual values of n calculated are 2·7 [from (1) and (2)], 2·65 [from (1) and (3)], 2·7 [from (1) and (4)], 2·65 [from (2) and (3)], 2·85 [from (2) and (4)], and 2·9 [from (3) and (4)].   It is seen that n approaches closely to the value 3, and the velocity coefficient k_1 varies, therefore, as the cube of the concentration of oxalic acid.

To sum up, the oxidation of oxalic acid by chromic acid is unimolecular with respect to chromic acid and termolecular with respect to oxalic acid, and consequently the whole reaction is quadrimolecular.   The course of the change may accordingly be represented by the equation:

$$H_2Cr_2O_7 + 3H_2C_2O_4 = Cr_2O_3 + 4H_2O + 6CO_2.$$

The neutralisation of chromium oxide (Cr_2O_3) by oxalic acid is probably extremely rapid, and in this case would not affect the velocity of the reaction.

In order to study the effect of change in the concentration of chromic acid, further experiments were made at 25°, the results of which may be summarised as follows:

With $N/4$-oxalic acid.

Concentration of chromic acid	$N/200$	$N/100$	$N/50$
Value of k_1	0·0331	0·0317	0·0298

With $3N/20$-oxalic acid.

Concentration of chromic acid	$N/250$	$N/200$	$N/50$
Value of k_1	0·0106	0·0103	0·00837

It will be seen from the above figures that the value of the velocity coefficient k_1 appears to vary with the initial concentration of the chromic acid, becoming greater as the latter diminishes. This variation of k_1 cannot be ascribed either to varying ionisation or to any of the ordinary disturbing effects arising from the products of the reaction, since these would in general exert an influence during the course of the reaction, whereas the results recorded in Tables I to IV show that the value of k_1 is practically constant under these conditions.   The coefficient is obviously affected by some factor which remains constant during a particular series of experiments, but varies from one series to another.

Since the velocity coefficients fall off as the concentration of chromic acid is increased, it does not appear justifiable to apply any of the methods for determining the order of the reaction

which are based on varying dilution, since these assume that the velocity coefficient is intrinsically independent of concentration, whereas the course of the reaction may be disturbed by secondary causes. Thus the well-known formula of Noyes,

$$m = 1 + \log\frac{t_1}{t_2} \Big/ \log\frac{c_2}{c_1},$$

is derived by integration from the differential velocity equation $-dc/dt = kc^m$, on the assumption that the velocity k is independent of the concentration. In some subsequent experiments it will be shown that chromium salts, which are a product of the reaction, have practically no effect on the velocity. It has been assumed that the action of chromium oxide (Cr_2O_3) on oxalic acid is practically instantaneous. This would be the case if the oxalic acid were in very large excess; but when the oxalic acid is not in very large excess this neutralisation may have a definite velocity, which would affect the kinetics of the whole reaction, producing a retarding effect on the chemical change. This is probably the explanation of the fall in the velocity coefficient with the increase in the concentration of chromic acid.

In order to determine the temperature coefficient of the reaction, measurements were made at different temperatures. Typical examples of the results obtained are recorded in detail in Tables V and VI.

TABLE V.

$N/10$-oxalic acid and $N/200$-chromic acid.

At 25°.

Time in minutes.	C.c. of Thiosulphate.	k_1.
0	16·65	—
43·25	11·25	0·00393
89	7·55	0·00386
130·25	5·35	0·00378
191	3·3	0·00368
248	2·05	0·00367
	Mean	0·00378

TABLE VI.

At 35°.

0	16·6	—
21·15	11·35	0·00780
41	8·15	0·00753
73	4·95	0·00719
90	3·8	0·00711
106	3·05	0·00695
	Mean	0·00732

Hence temperature coefficient for 10° rise $= k_{t+10}/k_t = 1·94$.

The results of other measurements with oxalic and chromic acids at different temperatures are summarised below:

$N/20$-oxalic acid and $N/200$-chromic acid.

Temperature.	Mean k_1.	k_{t+10}/k_t.
25°	0·000650 ⎱	1·95
35°	0·001269 ⎰	

$3N/20$-oxalic acid and $N/200$-chromic acid.

25°	0·0103 ⎱	1·93
35°	0·0198 ⎰	

$N/10$-oxalic acid and $N/100$-chromic acid.

25°	0·00346 ⎱	1·90
40°	0·00906 ⎱	1·80
50°	0·0162 ⎰	
60°	0·0279 ⎰	1·72

$N/20$-oxalic acid and $N/100$-chromic acid.

25°	0·000562 ⎱	1·90
40°	0·00149 ⎱	1·83
50°	0·00272 ⎰	
60°	0·00472 ⎰	1·72

Applying the Arrhenius formula, $\log k_1/k_2 = A(T_1 - T_2)/T_1 T_2$, to the results for (a) $N/10$-oxalic acid and $N/100$-chromic acid and (b) $N/20$-oxalic acid and $N/100$-chromic acid, we obtain the following results:

		(a) A = 2600		(b) A = 2613	
Temperature.	k (found).		k (calc.)	k (found).	k (calc.)
25°	(0·00346)		(0·00346)	(0·000566)	(0·000566)
40°	(0·00906)		(0·00906)	(0·00149)	(0·00149)
50°	0·0163		0·0163	0·00272	0·00270
60°	0·0280		0·0281	0·00472	0·00476

The next point investigated was the effect of sulphuric acid on this reaction, and measurements were made at different temperatures with different concentrations of sulphuric acid. The following is a summary of the results obtained:

$N/20$-oxalic acid and $N/100$-chromic acid.

Concentration of H_2SO_4...	0	$N/50$	$N/20$	$N/10$
k_1 at 25°	0·000562	0·000796	0·00105	0·00128

Concentration of H_2SO_4...	$N/5$	$3N/5$	$8N/5$	$4/N$
k_1 at 25°	0·00153	0·00149	0·000890	0·000357

$N/10$-oxalic acid and $N/100$-chromic acid

Concentration of H_2SO_4	0	$N/5$	$7 N/2$
k_1 at 25°	0·00346	0·00644	0·00140

Hence it appears that sulphuric acid at moderate concentrations accelerates the reaction, and in large excess retards it.

In order to determine the temperature coefficient of the oxidation of oxalic acid by chromic acid in the presence of sulphuric acid, measurements were made at 40° and 50°, and the following is a summary of the results:

$3N/20$-oxalic acid, $N/100$-chromic acid, and $N/5$-sulphuric acid.

Temperature.	Mean k_1.	k_{t+10}/k_t.
25°	0·01412 ⎫	1·86
50°	0·0665 ⎭	

$N/10$-oxalic acid, $N/100$-chromic acid, and $N/5$-sulphuric acid.

25°	0·00644 ⎫	1·87
50°	0·0309 ⎭	

$N/20$-oxalic acid, $N/100$-chromic acid, and $N/10$-sulphuric acid.

25°	0·00128 ⎫	1·85
50°	0·00594 ⎭	

$N/20$-oxalic acid, $N/100$-chromic acid, and $N/5$-sulphuric acid.

25°	0·00153 ⎫	1·84
50°	0·00699 ⎭	

The temperature coefficient of the oxidation of oxalic acid by chromic acid without sulphuric acid is 1·85. It appears, therefore, that the temperature coefficient remains unaltered in the presence of a small amount of sulphuric acid.

In order to determine the temperature coefficient in the presence of an excess of sulphuric acid, measurements were made at 40°. It has already been pointed out that in large excess, sulphuric acid acts as a negative catalyst in the oxidation of oxalic acid by chromic acid. The results are summarised as follows:

$N/10$-oxalic acid, $N/100$-chromic acid, and $7N/2$-sulphuric acid.

Temperature	Mean k_1.	k_{t+10}/k_t.
25°	0·00140 ⎫	2·61
40°	0·00591 ⎭	

$N/20$-oxalic acid and $N/100$-chromic acid.

Concentration of H_2SO_4	0	$3 N/5$	$8 N/5$	$4 N$
k_1 at 40°	0·00149	0·00481	0·00318	0·00156
Temperature coefficient	1·90	2·18	2·34	2·67

From the foregoing results, it appears that in the presence of an excess of sulphuric acid the temperature coefficient is larger than that obtained in its absence, and the greater the concentration of the acid the greater is the value of the temperature coefficient.

Effect of Manganese Salts on the Oxidation of Oxalic Acid by Chromic Acid.

It has been observed that manganese salts markedly accelerate the oxidation of oxalic acid by chromic acid. A stock solution of recrystallised manganese sulphate was prepared and standardised by precipitating the manganese as carbonate by ammonium carbonate. The precipitate was allowed to remain at about 80° for two hours, then collected, heated in a porcelain crucible, and weighed as Mn_3O_4. $N/20$-oxalic acid and $N/100$-chromic acid were used in each experiment with different amounts of manganese sulphate, and measurements were made at 25°.

TABLE VII.

0·03926 gram of $MnSO_4$ in 500 c.c.

Time in minutes.	C.c. of thio-sulphate.	k_1 (unimolecular).	k_0 (x/t).
0	31·3	—	—
14	28·6	0·00279	0·20
43	22·1	0·00351	0·21
75	15·95	0·00390	0·21
106	10·75	0·00437	0·20
138	6·2	0·00509	0·18

TABLE VIII.

0·06544 gram of $MnSO_4$ in 500 c.c.

0	31·3	—	—
15	26·6	0·00470	0·31
30	21·5	0·00544	0·32
50	15·25	0·00624	0·32
65	11·4	0·00675	0·31
85	6·6	0·00795	0·29

TABLE IX.

0·13088 gram of $MnSO_4$ in 500 c.c.

0	31·3	—	—
11	25·35	0·00831	0·54
21	19·42	0·00987	0·56
31	14·1	0·01117	0·56
41	9·35	0·01280	0·54
52	4·8	0·01566	0·51

TABLE X.

0·19632 gram of $MnSO_4$ in 500 c.c.

Time in minutes.	C.c. of thio- sulphate.	k_1 (unimolecular).	k_0 (x/t).
0	31·3	—	—
9	24·75	0·01132	0·73
17	17·95	0·01420	0·78
25	11·9	0·01680	0·77
31	8·1	0·01893	0·75
37	4·8	0·02208	0·72

Assuming that the velocity is proportional to the concentration of manganese sulphate, the course of the reaction may be represented by the equation

$$-dc_1/dt = kc_1^m c_2^n . h,$$

where c_1 and c_2 represent the concentrations of chromic acid and oxalic acid respectively and h represents the concentration of manganese sulphate. If the concentration of oxalic acid is made large compared with that of chromic acid, the concentration of the former does not sensibly alter during the course of the reaction, and the equation takes the form

$$-dc_1/dt = (kc_2^n)c_1^m h = k_1 c_1^m,$$

where $k_1 = h . kc_2^n$; if $m = 1$, the reaction would be unimolecular, and on integrating we get $k_1 = 1/t \log c_0/c_1$, and, as a matter of fact, in the absence of manganese sulphate the reaction is unimolecular, as previously shown. If, on the other hand, $m = 0$, the expression becomes $-dc_1/dt = k_1$ or $c_1/t = k_1$, that is, if the velocity of the reaction were independent of the concentration of chromic acid, we should have $c_1/t = \text{const.}$ or $x/t = k_0$, where $x = $ difference in the thiosulphate readings.

In the foregoing Tables, the unimolecular coefficient and this new coefficient ($x/t = \text{const.}$) are both set out, and it is seen that the unimolecular coefficient, far from being constant, increases notably with the time, whilst this new coefficient is almost constant. Hence it appears that in the presence of manganese sulphate, the velocity of the oxidation is independent of the concentration of chromic acid.

Homogeneous reactions in which the velocity is independent of the concentration of one of the reacting substances are of rare occurrence. One case is described by Friend (T., 1906, **89**, 1096), who studied the reaction between hydrogen peroxide and potassium persulphate and found that the velocity was independent of the concentration of the peroxide provided the latter was present in large excess. Another case has been investigated by Steele (T.,

1907, **91**, 1641), who found that in the oxidation of hypophosphorous acid by iodine in the presence of hydrogen ions the reaction-velocity is independent of the iodine concentration. Such behaviour is usually attributed to complications due to the occurrence of consecutive reactions, and in the present case it appears that the reaction occurs in two stages, one very much faster than the other, and that the chromic acid does not take part in the slower or controlling reaction (compare Skrabal, *Zeitsch. anorg. Chem.*, 1904, **42**, 1; Jablczyński, *ibid.*, 1908, **60**, 38).

Although from the experiments recorded above it appears that the velocity of the oxidation of oxalic acid by chromic acid in the presence of manganese sulphate is independent of the concentration of chromic acid, yet, when the concentration of manganese sulphate is exceedingly small, the reaction appears to be unimolecular. The following Tables will indicate the results obtained with very small concentrations of manganese sulphate.

$N/20$-oxalic acid and $N/100$-chromic acid at 25° with

TABLE XI.			TABLE XII.		
(a) 0·00393 gram of $MnSO_4$ in 500 c.c.			(b) 0·00262 gram of $MnSO_4$ in 500 c.c.		
Time in minutes.	C.c. of thiosulphate.	k_1 (unimolecular).	Time in minutes.	C.c. of thiosulphate.	k_1 (unimolecular).
0	31·3	—	0	31·3	—
75	27·3	0·000790	86	27·2	0·000708
138	24·4	0·000783	160	24·2	0·000698
188	22·4	0·000773	240	21·5	0·000679
245	20·35	0·000763	356	18·35	0·000651

In the following experiments, the joint effect of both sulphuric acid and manganese sulphate was studied at 25°.

$N/20$-oxalic acid, $N/100$-chromic acid, and $N/20$-sulphuric acid.

TABLE XIII.				TABLE XIV.			
With 0·06544 gram of $MnSO_4$ in 500 c.c.				With 0·01309 gram of $MnSO_4$ in 500 c.c.			
0	33·6	—	—	0	33·6	—	—
10	30·2	0·00463	0·34	15	31·35	0·00200	0·15
30	21·0	0·00680	0·42	37	28·2	0·00206	0·15
45	14·95	0·00781	0·41	72	23·6	0·00213	0·14
63	8·95	0·00911	0·40	132	17·0	0·00224	0·13
85	3·0	0·01234	0·36	—	—	—	—

Hence, even in the presence of sulphuric acid the reaction velocity is independent of the concentration of chromic acid.

In order to determine the temperature coefficient of the oxida-

tion of oxalic acid by chromic acid in the presence of manganese sulphate, measurements were made at various temperatures.

$N/20$-Oxalic acid and $N/100$-chromic acid were used in each experiment with different quantities of manganese sulphate.

TABLE XV.

With 0·02617 gram of $MnSO_4$ in 500 c.c.

At 25°.				At 40°.			
Time in minutes.	C.c. of thio- sulphate.	k_1 (unimole- cular).	$k_0(x/t)$.	Time in minutes.	C.c. of thio- sulphate.	k_1 (unimole- cular).	$k_0(x/t)$.
0	33·3	—	—	0	33·3	—	—
20	30·28	0·00206	0·15	8	27·27	0·0108	0·75
50	25·0	0·00249	0·16	18	19·95	0·0123	0·74
78	20·65	0·00265	0·16	27	14·2	0·0137	0·71
115	15·35	0·00292	0·16	35	9·68	0·0153	0·68
144	10·4	0·00351	0·16	45	4·9	0·0184	0·64
		Mean.........	0·16			Mean.........	0·70

Therefore $k_{t+10}/k_t = 2·67$.

TABLE XVI.

With 0·7050 gram of $MnSO_4$ in 500 c.c.

At 0°.				At 25°.			
Time in minutes.	C.c. of thio- sulphate.	k_1 (unimole- cular).	$k_0(x/t)$.	Time in minutes.	C.c. of thio- sulphate.	k_1 (unimole- cular).	$k_0(x/t)$.
0	33·3	—	—	0	33·3	—	—
60	26·9	0·00154	0·107	4	27·5	0·0207	1·45
120	19·3	0·00195	0·117	12	12·65	0·0350	1·72
175	14·05	0·00214	0·110	16	7·8	0·0394	1·60
225	10·9	0·00215	0·100	20	4·8	0·0420	1·42
275	8·0	0·00225	0·092	—	—	—	—
		Mean	0·105			Mean	1·55

Therefore k_{t+10}/k_t between 0° and 25° $= 2·93$.

As has been previously observed, in the presence of manganese sulphate the oxidation of oxalic acid by chromic acid is independent of the concentration of the latter. Hence the reaction becomes of an order lower than that of the reaction in the absence of manganese salts. It is well known that reactions in which one or two molecules take part have larger temperature coefficients than those of reactions of higher order (compare Halban, *Zeitsch. physikal. Chem.*, 1909, **67**, 129).

The temperature coefficient of the oxidation of oxalic acid by chromic acid is 1·94 between 25° and 40°, whilst in the presence of manganese salts it is 2·68 between 25° and 40° and 2·95 between 0° and 25°, agreeing with other known examples.

Effect of Other Catalysts on the Oxidation of Oxalic Acid by Chromic Acid.

Summary of results obtained with $N/10$-oxalic acid and $N/100$-chromic acid and different concentrations of molybdic acid:

Concentration of molybdic acid	0	0·0063	0·0082	0·01367
k_1 at 25°	0·00353	0·00173	0·00145	0·00086
Temperature coefficient ...	1·92	1·99	2·0	2·05

From the above figures it appears that the negative catalyst, molybdic acid, produces an increase in the value of the temperature coefficient.

Summary of results obtained with ammonium molybdate as a catalyst with $N/10$-oxalic acid and $N/100$-chromic acid:

Molar concentration of molybdate	0	0·000463	0·000926	0·002315
k_1 at 25°	0·00353	0·00245	0·00180	0·000766
Temperature coefficient ...	1·92	1·99	2·01	2·08

Summary of results with boric acid as a catalyst with $N/10$-oxalic acid and $N/100$-chromic acid:

Concentration of boric acid	0	0·01434	0·0358	0·0716	0·216	0·432
k_1 at 25°	0·00353	0·00343	0·00317	0·00283	0·00207	0·00138
Temperature coefficient	1·92	1·95	1·99	2·0	2·11	2·24

Both ammonium molybdate and boric acid are retarders. The greater the retardation the greater is the value of the temperature coefficient.

Formic Acid and Chromic Acid.

Formic acid can also be oxidised by chromic acid; at equal concentrations the velocity of the oxidation of formic acid is decidedly smaller than that of the oxidation of oxalic acid. Hence, in measuring the velocity at 25°, fairly concentrated solutions of formic acid have been used. The experimental method is the same as in the oxalic acid oxidation; since formic acid is volatile, especially at the higher experimental temperatures, tightly fitting stoppered Jena-glass bottles were used as reaction vessels. Kahlbaum's pure formic acid was used throughout the measurements. From a concentrated stock solution of 15 litres, suitably diluted solutions were prepared. In this case, also, the free chromic acid in the reaction mixture was estimated from time to time by the iodometric method, and the amounts of sodium thiosulphate required are recorded in the tables. From comparative experiments it was first established that the presence of free formic acid or oxalic acid did not interfere with the accuracy of the estima-

tion of chromic acid by the iodometric method; as a rule, in the estimation of chromic acid by this method, an excess of hydrochloric acid was used, and the velocity of the oxidation of formic or oxalic acid by iodine, especially in the presence of hydrochloric acid, is negligible. The velocity of the reaction may be represented by the equation $-dc_1/dt = kc_1^m c_2^n$, where c_1 and c_2 denote concentrations of chromic and formic acids respectively.

Determination of m.—In the following series of experiments, the formic acid used was in large excess, and hence the concentration may be taken as practically constant during the course of the reaction; the velocity equation takes the following form: $-dc_1/dt = (kc_2^n)c_1^m = k_1 c_1^m$, where $k_1 = kc_2^n$. Hence the order of the reaction is the same as m.

The results recorded in the following Tables were all obtained at 25°.

TABLE I.

6·166 N-formic acid and $N/30$-chromic acid.

Time in minutes.	C.c. of thio-sulphate.	$k_1 = 1/t \log c_0/c.$
0	52·1	—
95	26·55	0·00308
135	19·95	0·00309
200	12·6	0·00308
275	7·4	0·00308
330	5·0	0·00308
	Mean......	0·00308

TABLE II.

3·083 N-formic acid and $N/30$-chromic acid.

Time in minutes.	C.c. of thio-sulphate.	k_1.
0	52·1	—
135	45·15	0·000460
285	38·5	0·000460
525	29·65	0·000466
1416	11·55	0·000462
1817	7·6	0·000460
	Mean......	0·000462

TABLE III.

2·466 N-formic acid and $N/30$-chromic acid.

0	56·1	—
240	49·0	0·000245
475	42·9	0·000245
1345	26·6	0·000241
1907	19·0	0·000247
	Mean......	0·000245

TABLE IV.

2·966 N-formic acid and $N/30$-chromic acid

0	55·4	—
155	47·8	0·000413
335	40·25	0·000412
555	32·8	0·000410
1360	15·2	0·000413
	Mean......	0·000412

TABLE V.

5·933 N-formic acid and $N/30$-chromic acid.

0	56·1	—
83	33·0	0·00277
130	24·75	0·00273
170	19·2	0·00274
227	13·3	0·00275
	Mean......	0·00275

TABLE VI.

2·3733 N-formic acid and $N/30$-chromic acid.

0	56·1	—
247	49·5	0·000220
504	43·4	0·000221
1450	27·0	0·000219
1990	20·45	0·000220
	Mean......	0·000220

From the foregoing results it appears that the values of k_1 calculated for $m=1$ exhibit such a degree of constancy that the equation indicating a unimolecular reaction may fairly be regarded as the appropriate one. Hence, in the presence of an excess of formic acid, the oxidation is a unimolecular reaction.

Determination of n.—The "isolation method" is also used in this oxidation. Supposing that k_1' and k_1'' are the values of k_1 (in the equation $k_1 = kc^n$) obtained in two experiments, in each of which the initial concentration of chromic acid is the same, whilst the concentrations of formic acid are different, say c_2' and c_2'', the following equations are obtained: $k_1' = kc_2'^n$, $k_1'' = kc_2''^n$, whence

$$n = \log \frac{k_1'}{k_1''} \Big/ \log \frac{c_2'}{c_2''}.$$

On comparing the Tables I—VI, the following results are obtained:

Concentration of	(1)	(2)	(3)	(4)	(5)	(6)
formic acid ...	6·166	3·083	2·466	2·966	5·933	2·373
k_1 at 25°	0·00308	0·000462	0·000245	0·000412	0·00275	0·000220

It is evident that the value of k_1 decreases rapidly as the concentration of formic acid diminishes, which indicates a high value for the exponent n. The actual values of n obtained by combining these results are 2·7, 2·8, 2·75, 2·96, 2·8, 2·85, 2·96, 2·75, 2·84, 2·75, 2·8, 2·75, 2·8, and 2·76. It is seen that n approaches closely to the value 3, and the velocity coefficient k_1 varies, therefore, as the cube of the concentration of formic acid.

To sum up, the oxidation of formic acid also is unimolecular with regard to chromic acid and termolecular with respect to formic acid, and consequently the whole reaction is quadrimolecular. The course of the change may accordingly be represented by the equation

$$H_2Cr_2O_7 + 3H \cdot CO_2H = Cr_2O_3 + 6H_2O + 3CO_2.$$
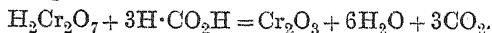
The action of chromium oxide (Cr_2O_3) on formic acid may be assumed to be extremely rapid and to be without effect on the velocity of the reaction. From the kinetic measurements it is seen that only one molecule of chromic acid takes part in the reaction, and consequently these measurements support the view that the formula of chromic acid is $H_2Cr_2O_7$ and not H_2CrO_4; had it been H_2CrO_4, two molecules of chromic acid should have taken part in the reaction (compare Datta and Dhar, *J. Amer. Chem. Soc.*, 1916, **38**, 1303).

In order to study the effect of change in the concentration of chromic acid, further experiments were made at 25°, the results of which may be summarised as follows;

With $3·083$ N-formic acid.

Concentration of chromic acid	$N/15$	$N/30$	$N/60$
k_1 at $25°$	0·000461	0·000462	0·000462

With $2·966$ N-formic acid.

Concentration of chromic acid	$N/30$	$N/60$
k_1 at $25°$	0·000413	0·000412

Hence in this reaction, if we use an excess of formic acid and vary the concentration of chromic acid, we find that the unimolecular coefficient does not change with the chromic acid concentration. In the presence of an excess of formic acid, therefore, the reaction is strictly unimolecular and there are no disturbing factors.

In order to determine the temperature coefficients of the reaction, measurements were made at different temperatures. Typical examples of the results obtained are recorded in detail in Tables VII, VIII, and IX.

TABLE VII.

$2·966$ N-Formic acid and $N/30$-chromic acid were used in each experiment:

At 40°.

$t.$	$a-x.$	$k_1.$	
0	57·1	—	
105	42·3	0·00124	
195	32·5	0·00125	
300	24·5	0·00122	Table IV gives k_1 at $25° = 0·000412$.
425	17·25	0·00122	Therefore $k_{t+10}/k_t = 2·07$.
495	14·05	0·00123	

Mean...... 0·00123

TABLE VIII.

At 50°.

0	55·35	—	
40	43·95	0·00256	
90	33·05	0·00248	From Tables VII and VIII we get
152	22·85	0·00252	k_{t+10}/k_t between $40°$ and $50° =$
214	16·35	0·00250	$2·02$.
266	12·0	0·00250	

Mean...... 0·00250

TABLE IX.

At 60°.

0	57·0	—	
37	37·7	0·00485	
71	25·9	0·00482	From Tables VIII and IX we get
105	17·95	0·00477	k_{t+10}/k_t between $50°$ and $60° =$
153	10·7	0·00474	$1·9$.

Mean...... 0·00479

Applying the Arrhenius formula $\log k_1'/k_1'' = A \cdot (T_1 - T_2)/T_1 T_2$, we get the value of $A = 3015$.

Temperature.	k_1 (obs.).	k_1 (calc.).
25°	(0·000412)	(0·000412)
40°	0·00123	0·000125
50°	(0·00250)	(0·00250)
60°	0·00479	0·00476

In order to study the effect of change in the concentration of formic acid on the temperature coefficient, measurements were made with different concentrations of formic acid and $N/30$-chromic acid, and the results obtained are summarised below:

5·933 N-formic acid	Temperature interval	25—40°	40—60°	
	Temperature coefficient	2·05	1·91	

3·083 N-formic acid	Temperature interval	25—35°	25—50°	
	Temperature coefficient	2·09	2·03	

2·966 N-formic acid	Temperature interval	25—40°	40—50°	50—60°
	Temperature coefficient	2·07	2·02	1·90

1·186 N-formic acid	Temperature interval	—	40—50°	50—60°
	Temperature coefficient	—	2·01	1·90

From the above figures it appears that change in the concentration of formic acid has no appreciable effect on the temperature coefficient.

Effect of Sulphuric Acid.—The effect of sulphuric acid was studied at various temperatures with different concentrations of the acid. Typical examples of the results obtained are recorded in Table X.

TABLE X.

3·083 N-Formic acid, $N/30$-chromic acid, and $N/6$-sulphuric acid.

	At 25°.				At 50°.	
t.	$a-x$.	k_1.		t.	$a-x$.	k_1.
0	55·9	—		0	55·9	—
117·5	40·4	0·00120		24	40·8	0·00570
219	30·8	0·00118		44·3	31·2	0·00572
350	21·6	0·00118		60	25·4	0·00571
462	15·6	0·00120		90	17·1	0·00571
	Mean......	0·00119			Mean......	0·00571

Therefore $k_{t+10}/k_t = 1·87$.

Summary of results obtained with 3·083 N-formic acid and $N/30$-chromic acid:

Concentration of H_2SO_4	0	$N/6$	$N/3$	$2N/3$
k_1 at 25°	0·000462	0·00119	0·00262	0·00603
Temperature coefficient between 25° and 50°	2·03	1·87	1·86	1·84

From the foregoing results it appears that in the presence of sulphuric acid the oxidation of formic acid by chromic acid is greatly accelerated and has a lower value for its temperature coefficient, and the greater the concentration of sulphuric acid the greater is the fall. Experiments were made with other concentrations of formic acid, using sulphuric acid as an accelerator. A summary of the results obtained will be found in the following Tables. In each case $N/30$-chromic acid was used.

TABLE XI.

Concentration of formic acid.	Concentration of sulphuric acid.	Mean k_1 at 25°.	Mean k_1 at 50°.	k_{t+10}/k_t.
1·233 N	0	0·000055	0·000330	2·04
1·233 N	$N/6$	0·000348	0·00162	1·85
1·233 N	$N/3$	0·000766	0·00356	1·84
1·233 N	$3N/5$	0·00161	0·00724	1·83
0·616 N	0	0·0000092	0·000055	2·04
0·616 N	$N/6$	0·000144	0·000673	1·85
0·616 N	$N/3$	0·000320	0·00148	1·84
0·616 N	$2N/3$	0·000748	0·00340	1·83

TABLE XII.

Concentration of formic acid.	Concentration of sulphuric acid.	Mean k_1 at 25°.	Mean k_1 at 40°.	k_{t+10}/k_t.
1·186 N	0	0·0000515	0·000154	2·07
1·186 N	$N/5$	0·000304	0·000802	1·91
1·186 N	$3N/5$	0·00122	0·00317	1·89
1·186 N	$6N/5$	0·00373	0·00948	1·85
0·593 N	0	0·0000084	0·0000251	2·07
0·593 N	$N/3$	0·000253	0·000662	1·90
0·593 N	$19N/15$	0·00112	0·00291	1·88

From all these results it is seen that there is a slight fall in the temperature coefficient with the increase in the concentration of sulphuric acid.

The next point investigated was the effect of manganese sulphate on the oxidation of formic acid by chromic acid. From qualitative experiments it was observed that manganese salt was a retarder in this reaction, whilst it had been previously shown that it is a great accelerator in the oxidation of oxalic acid by chromic acid.

TABLE XIII.

At 50°.

6·166 N-Formic acid, $N/30$-chromic acid, and 0·000164 gram of MnSO$_4$. Volume of mixture = 150 c.c.

t.	$a-x$.	k_1.
0	51·8	—
20	28·08	0·0133
39	15·8	0·0132
77	4·85	0·0133
87	3·6	0·0133

Mean...... 0·0133

k_1 at 50° without any manganese sulphate = 0·0177; hence this reaction is very susceptible to the retarding influence of manganese sulphate even in very small concentration. The following is the summary of results obtained with 6·166 N-formic acid and $N/30$-chromic acid at 50° with different concentrations of manganese sulphate:

Gram of MnSO$_4$	0	0·000164	0·01636	0·0654	0·0819	0·3272
k_1 at 50°	0·0177	0·0133	0·00763	0·00675	0·00661	0·00627

From the summary, it is seen that the greater the amount of manganese sulphate the greater is the retardation.

The following is the summary of results obtained with 3·083 N-formic acid and $N/30$-chromic acid at 50°:

Gram of MnSO$_4$...	0	0·0000164	0·000164	0·00164
k_1 at 50°	0·00272	0·00264	0·00225	0·00154

Hence it is seen that the oxidation of formic acid by chromic acid is extremely sensitive to the retarding influence of manganese sulphate, so much so that 0·0000164 gram of manganese sulphate in 150 c.c. appreciably affects the velocity coefficients.

In order to determine the temperature coefficient of the oxidation of formic acid by chromic acid in the presence of manganese sulphate, experiments were made at several temperatures. Typical results are given in the following Table.

TABLE XIV.

3·083 N-Formic acid, $N/30$-chromic acid, and 0·02617 gram of MnSO$_4$. Volume of mixture = 150 c.c.

At 25°.			At 35°.		
t.	$a-x$.	k_1.	t.	$a-x$.	k_1.
0	44·0	—			
385	37·15	0·000190	0	54·75	—
1366	24·3	0·000189	190	45·9	0·000403
1610	21·88	0·000188	380	38·7	0·000396
1815	19·95	0·000189	1395	15·2	0·000398
2870	12·50	0·000189	1675	11·8	0·000397

Mean...... 0·000189   Mean...... 0·000398

Therefore $k_{t+10}/k_t = 2.10$; the temperature coefficient without any manganese salt is 2.09. Hence in the presence of manganese sulphate the temperature coefficient remains unaltered. The following is a summary of the results obtained with 6.166 N-formic acid and $N/30$-chromic acid with different concentrations of manganese sulphate:

Gram of $MnSO_4$	0	0.0654	0.0819	0.3272
k_1 at 25°	0.00308	0.00115	0.00112	0.00106
Temperature coefficient between 25° and 50°	2.03	2.03	2.03	2.03

The following Table summarises the results obtained with 2.966 N-formic acid and $N/30$-chromic acid with greater concentrations of manganese sulphate.

TABLE XV.

Grams of $MnSO_4$.	Mean k_1 at 25°.	Mean k_1 at 50°.	k_{t+10}/k_t.
0	0.000413	0.00250	2.05
1.1750	0.000141	0.000841	2.04
1.7625	0.000122	0.000734	2.05
2.3500	0.000136	0.000809	2.04
3.5250	0.000138	0.000810	2.03
5.8750	0.000142	0.000860	2.05
11.7500	0.000172	0.000970	2.0

It appears from the foregoing results that the temperature coefficient in the presence of the negative catalyst, manganese sulphate, does not change. Also it is seen that if the concentration of manganese sulphate is increased, the velocity coefficient falls off to a certain limiting value and then increases with the increase in the concentration of the catalyst.

The joint effect of sulphuric acid and manganese sulphate on the oxidation of formic acid by chromic acid was also investigated at 50°.

TABLE XVI.

1.233 N-Formic acid and $N/30$-chromic acid. Volume of mixture $= 150$ c.c.

(a) With 0.01309 gram of $MnSO_4$.

t.	$a-x$.	k_1.
0	55.6	—
406	46.9	0.000182
1445	30.5	0.000180
1920	25.1	0.000180
3025	15.85	0.000180
4325	9.1	0.000182
Mean.........		0.000181

(b) With 0.01309 gram of $MnSO_4$ and $N/3$-sulphuric acid.

t.	$a-x$.	k_1.
0	55.6	—
41	47.35	0.00170
121	34.65	0.00170
265	20.0	0.00168
331	15.25	0.00168
413	11.2	0.00169
Mean.........		0.00169

k_1 without any sulphate $= 0.000330$, whilst k_1 with $N/3$-sulphuric acid but no manganese sulphate $= 0.00356$. Consequently even in the presence of the accelerator, sulphuric acid, manganese sulphate has a retarding effect.

Next, the effect of manganese chloride was studied. The salt was purified by crystallisation from water. The following is a summary of the results obtained with manganese chloride as a catalyst and 3.083 N-formic acid and $N/30$-chromic acid:

Concentration of $MnCl_2$	0	0.0018	0.0090	0.0179	0.0359
k_1 at 25°	0.000462	0.000205	0.000190	0.000179	0.000169
Temperature coefficient between 25° and 40°	2.06	2.10	2.11	2.12	2.14
Concentration of $MnCl_2$	0.0718	0.1795	0.359	0.718	
k_1 at 25°	0.000164	0.000180	0.000207	0.000300	
Temperature coefficient between 25° and 40°	2.14	2.16	2.15	2.14	

Hence manganese chloride, like manganese sulphate, even in dilute solutions, produces a marked retarding effect on this reaction. If the concentration of the manganese salt is increased, the velocity coefficient falls off to a minimum and then increases with the increase in the concentration of the catalyst. This peculiar behaviour of the catalyst in fairly dilute solutions (for example, the maximum concentration used is 0.718 N) is seldom encountered (compare Tubandt, *Annalen*, 1905, **339**, 41; 1907, **354**, 259; 1910, **377**, 284).

Moreover, it will be seen from the foregoing summary that the temperature coefficient in the presence of the negative catalyst is appreciably higher than that obtained without any manganese chloride.

It is known that molybdic acid is a powerful catalyst in some oxidations, and its effect on this reaction was studied, $N/30$-chromic acid being used in each experiment.

Concentration of formic acid.	Molar concentration of molybdic acid.	Mean k_1 at 25°.	Mean k_1 at 40°.	k_{t+10}/k_t.
$2.966N$	0	0.000412	0.00123	2.07
,,	0.005	0.000416	0.00125	2.08

Hence molybdic acid acts as a weak positive catalyst on the oxidation of formic acid by chromic acid, whilst it has been shown previously that in the oxalic acid oxidation it is a negative catalyst.

Sodium Formate and Iodine.

Formates are easily oxidised by iodine at the ordinary temperature, and this reaction has a conveniently measurable velocity. The course of the reaction is represented by the equation:

$$H \cdot CO_2Na + I_2 = NaI + HI + CO_2.$$
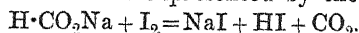
The hydrogen ions formed as a product of the change greatly retard the reaction, and in order to avoid their formation an excess of a salt of a weak acid (for example, sodium acetate) was always used; in this way the course of the reaction became regular.

Ordinary pure iodine was mixed with a little potassium iodide and was allowed to sublime very slowly. This product was again sublimed. Schuchardt's pure sodium formate was recrystallised from water. A standard solution was prepared by evaporating a measured volume of the solution in a platinum crucible, heating the residue with sulphuric acid, and weighing the sodium sulphate formed. The potassium iodide used was twice crystallised from water and dissolved in water free from oxygen. The solution of the iodide was standardised by weighing the silver iodide obtained from a known volume of the solution.

In order to avoid loss of iodine by volatilisation, tightly fitting stoppered Jena-glass bottles were used as reaction vessels. From time to time measured volumes were withdrawn from the reaction vessel, which was placed in a thermostat at a constant temperature, and were allowed to run into ice-cold distilled water to stop the reaction, and the free iodine was immediately titrated by standard thiosulphate. The velocity of the reaction may be represented by the equation $-dc_1/dt = kc_1^m c_2^n$, where c_1 and c_2 are the concentrations of iodine and formate respectively. Since iodine dissolves very sparingly in water, in order to prepare a moderately concentrated solution potassium iodide must be used. It is well known that in a potassium iodide solution of iodine there is the following equilibrium, $KI_3 \rightleftharpoons KI + I_2$, and the greater part of the dissolved iodine exists as KI_3. Hence, even if a large excess of sodium formate in comparison with the total iodine is not used, owing to the presence of potassium iodide, the concentration of free iodine is much diminished, and the concentration of formate is actually large in comparison with that of free iodine. Consequently the velocity equation takes the following form: $-dc_1/dt = (kc_2^n)c_1^m = k_1 c_1^m$, where $k_1 = kc_2^n$. The order of the reaction is therefore the same as m.

In the three following Tables 1·27 grams of iodine and 5·4132 grams of potassium iodide were used with different concentrations of sodium formate, and the measurements were made at 25°; the total volume of the mixture was 150 c.c.

TABLE I.		
3·4004 Grams of sodium formate.		
Time in minutes.	C.c. of thio-sulphate.	$k_1 = 1/t\log c_0/c.$
0	76·0	—
24	68·0	0·00201
60	57·6	0·00201
91	49·65	0·00203
141	41·0	0·00190
174	36·1	0·00186
Mean.........		0·00196

TABLE II.		
1·7002 Grams of sodium formate.		
Time in minutes.	C.c. of thio-sulphate.	$k_1 = 1/t\log c_0/c.$
0	79·0	—
45	71·1	0·00101
115	60·6	0·00100
188	51·95	0·00097
279	43·5	0·00093
360	37·4	0·00090
509	28·7	0·00086
Mean.........		0·000945

TABLE III.		
0·6801 Gram of sodium formate.		
0	79·0	—
100	72·3	0·000385
250	63·3	0·000384
480	51·9	0·000380
1440	23·15	0·000370
Mean.........		0·000380

In all these measurements 4·22 grams of sodium acetate were used in each experiment. In the Tables IV, V, VI, and VII 0·635 gram of iodine and 2·7006 grams of potassium iodide were used in each observation at 25° with different concentrations of sodium formate, and the total volume was always 150 c.c.

TABLE IV.		
6·8008 Grams of sodium formate.		
0	39·5	—
10	32·7	0·00821
25	24·75	0·00812
52	15·85	0·00762
78	10·65	0·00729
Mean.........		0·00781

TABLE V.		
3·4004 Grams of sodium formate.		
0	39·5	—
30	29·7	0·00412
71	21·2	0·00380
106	16·2	0·00365
130	13·6	0·00356
Mean.........		0·00378

TABLE VI.		
1·7002 Grams of sodium formate.		
0	39·5	—
50	31·5	0·00196
100	25·3	0·00193
140	21·5	0·00188
201	17·15	0·00180
285	12·6	0·00174
Mean.........		0·00186

TABLE VII.		
0·6801 Gram of sodium formate.		
0	39·5	—
100	32·93	0·000790
200	27·7	0·000770
390	20·0	0·000758
520	16·1	0·000750
Mean.........		0·000767

From the foregoing Tables it is seen that, in spite of a slight tendency to fall off, the values of k_1 calculated for $m = 1$ exhibit such a degree of constancy that the equation indicating a unimolecular reaction may fairly be regarded as the appropriate one.

Determination of n.—Supposing that k_1' and k_1'' are the values of k_1 (in the equation $k_1 = kc^n$) obtained in two experiments, in each of which the initial concentration of iodine is the same, whilst the concentrations of sodium formate are different, say c_2' and c_2'', the following equations are obtained: $k_1' = kc_2'^n$; $k_1'' = kc_2''^n$, whence $n = \log \dfrac{k_1'}{k_1''} \bigg/ \log \dfrac{c_2'}{c_2''}$. On comparing the foregoing Tables, the following summary of results is obtained:

A.

Grams of formate	3·4004	1·7002	0·6801	(1·27 grams of iodine and 5·4132 grams of potassium iodide.
k_1 at 25°	0·00196	0·000945	0·000380	

B.

Grams of formate	6·8008	3·4004	1·7002	0·6801	(0·635 gram of iodine and 2·7066 grams of potassium iodide.
k_1 at 25°	0·00781	0·00378	0·00186	0·000767	

The actual values of n obtained in A are 1·05, 1·02, and 0·99, and from B the values are 1·04, 1·03, 1·01, 1·02, 0·99, and 0·97. It is seen that n approaches closely to the value 1, and the velocity coefficient k_1 varies, therefore, directly as the concentration of sodium formate.

To sum up, the oxidation of sodium formate by iodine is unimolecular with respect to both iodine and sodium formate, and consequently the reaction is bimolecular; this behaviour is expected from the chemical equation representing the change $H \cdot CO_2Na + I_2 = HI + NaI + CO_2$.

From the foregoing summary of results, it will be seen that iodine ions retard the reaction, and the slight lowering of the velocity coefficients as the reaction proceeds is due to the continued increase in the concentration of iodine ions, which are products of the reaction.

One peculiar point will be noticed, namely, that if there is a definite concentration of potassium iodide, the velocity coefficient does not depend on the concentration of iodine, but if we start with a definite concentration of iodine and increase the concentration of potassium iodide, the velocity coefficient falls off. This effect cannot be explained from the mass action equilibrium

$KI + I_2 \rightleftharpoons KI_3$.   In Table I we have 1·27 grams of iodine and 5·4132 grams of potassium iodide and k_1 at $25° = 0·00196$; and in Table V we have 0·635 gram of iodine and 2·7066 grams of potassium iodide and k_1 at $25° = 0·00378$. The concentrations of sodium formate in these two cases are equal, and according to the mass action equilibrium the velocity coefficient should be the same, since the ratio of the concentrations of potassium iodide and iodine is the same in the two cases.   This point has been thoroughly studied in the oxidation of sodium formate by mercuric chloride in the presence of several chlorides.

In order to determine the temperature coefficient of the oxidation of sodium formate by iodine, measurements were made at different temperatures.   Typical examples of the results obtained are recorded in the following Tables.

TABLE VIII.

3·4004 Grams of sodium formate, 1·27 grams of iodine, and 5·4132 grams of potassium iodide.   Volume = 150 c.c.

At 50°.

t.	$a-x$.	k_1.
0	98·7	—
4	57·3	0·0590
8	33·4	0·0588
12	19·5	0·0586
16	11·4	0·0585
Mean.........		0·0587

Table I gives k_1 at $25° = 0·00196$; therefore k_{t+10}/k_t between $25°$ and $50° = 3·89$.

TABLE IX.

0·6801 Gram of sodium formate, 1·27 grams of iodine, and 5·4132 grams of potassium iodide.   Volume = 150 c.c.

At 50°.

t.	$a-x$.	k_1.
0	98·7	—
5	86·35	0·0116
10	75·7	0·0115
18	62·05	0·0112
25	51·8	0·0112
35	40·7	0·0110
Mean.........		0·0113

Table III gives k_1 at $25° = 0·000390$; therefore k_{t+10}/k_t between $25°$ and $50° = 3·88$.

TABLE X.

6·8008 Grams of sodium formate, 0·635 gram of iodine, and 2·7066 grams of potassium iodide. Volume = 150 c.c.

At 35°.

t.	$a - x$.	k_1.
0	39·5	—
4	29·3	0·0325
10	19·0	0·0318
15	13·55	0·0310
20	10·05	0·0298
Mean.........		0·0313

Table IV gives k_1 at $25° = 0·00781$; therefore $k_{35}/k_{25} = 4·01$.

From the foregoing results, it is seen that the temperature coefficient of the oxidation of sodium formate by iodine is 4·01 between 25° and 35° and 3·89 between 25° and 50°.

It has already been observed that potassium iodide, or rather iodine ions, act as a negative catalyst in this reaction. In order to determine if there is any change in the temperature coefficient when the reaction is greatly retarded by potassium iodide, measurements were made at different temperatures with various concentrations of potassium iodide. The results obtained are as follows:

1·7002 grams of sodium formate and 0·3354 gram of iodine.	Grams of potassium iodide ...	1·6952	2·1708	9·9086
	k_1 at 25°	0·00297	0·000647	0·000470
	Temperature coefficient	4·01	4·19	4·13

1·7002 grams of sodium formate and 0·3354 gram of iodine.	Grams of potassium iodide ...	15·3843	31·8110
	k_1 at 25°	0·000320	0·000173
	Temperature coefficient	4·11	4·02

Hence, even in strongly catalysed reactions, the temperature coefficients are practically the same as those in the feebly catalysed ones.

A few more experiments were made with different concentrations of iodine and potassium iodide, and the experimental results are summarised in the following Tables.

TABLE XI.

1·7002 Grams of sodium formate, 0·1677 gram of iodine. Volume = 150 c.c.

Potassium iodide. Grams.	Mean k_1 at 25°.	Mean k_1 at 35°.	k_{t+10}/k_t.
0·8476	0·00556	0·0229	4·10
9·0610	0·000520	0·00211	4·06
29·8732	0·000205	0·000833	4·06
78·2492	0·000112	0·000413	3·69

TABLE XII.

0·6801 Gram of sodium formate, 0·1677 gram of iodine. Volume = 150 c.c.

Potassium iodide. Grams.	Mean k_1 at 25°.	Mean k_1 at 50°.	k_{t+10}/k_t.
0·8476	0·00212	0·0654	3·95
20·1080	0·000111	0·00342	3·93
29·8732	0·0000804	0·00242	3·90
40·2236	0·0000573	0·00152	3·71

In the results last recorded in this, as well as in the foregoing Table, the concentration of potassium iodide was very great; complexities due to changes of viscosity might have arisen and have caused the temperature coefficients to be lower than the other values in the same series. In this case, we find that the temperature coefficient of the reaction does not change in the presence of potassium iodide.

The effect of manganese sulphate was also studied, and the following is a summary of the results obtained:

Grams of manganese sulphate .	0	0·0524	0·1048	1·8882
Value of k_1 at 25°	0·00751	0·00749	0·00735	0·00634

Grams of manganese sulphate	6·294	12·588	18·882	37·764
Value of k_1 at 25°	0·00478	0·00376	0·00286	0·00151

Evidently the velocity coefficient falls off as the concentration of manganese salt is increased.

Sodium Formate and Mercuric Chloride.

It is well known that formic acid and formates can be oxidised by mercuric chloride. The mechanism of the reduction of mercuric chloride by formic acid and formates has been investigated by Portes and Ruyssen (*Compt. rend.*, 1876, **82**, 1504), Scala (*Gazzetta*, 1890, **20**, 393), Lieben (*Monatsh.*, 1893, **14**, 750), etc.

Recently Findlay and Davies (T., 1913, **103**, 1554) and Linhart (*J. Amer. Chem. Soc.*, 1915, **37**, 70) have also studied the problem. From the ordinary method of chemical dynamics they have found that the velocity coefficients follow the bimolecular law.

In order to determine the temperature coefficient and the effect of catalysts on this reaction the following experiments were made.

Since ordinary sodium formate contains a little sodium carbonate, a solution of the salt was carefully neutralised with pure formic acid, evaporated and crystallised. As a rule, the salt was twice crystallised from water and dried centrifugally. A solu-

tion was prepared and was standardised by estimating the formic acid with potassium permanganate, and this estimation was checked by evaporating a measured volume of the solution in a platinum crucible, heating the residue with sulphuric acid, and weighing the sodium sulphate formed. The other salts used were generally recrystallised twice. From time to time measured volumes were withdrawn by means of a pipette fitted with a plug of cotton wool, to keep back mercurous chloride, and run into a known volume of potassium iodide; the excess of potassium iodide was then titrated against standard mercuric chloride. It was seen from preliminary work that this method of estimation was quite accurate.

The equation representing the chemical change is the following:
$$2HgCl_2 + H \cdot CO_2Na = 2HgCl + NaCl + HCl.$$
The hydrogen ions formed in the reaction greatly retard the change. In order to avoid this difficulty, $2 \cdot 11$ grams of sodium acetate were added to the reacting mixtures.
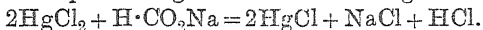
The velocity of the reaction may be represented by an equation of the form $-dc_1/dt = kc_1{}^m c_2{}^n$, where c_1 and c_2 represent concentrations of mercuric chloride and formate respectively.

Determination of m.—In the following series of experiments, the sodium formate used was in large excess, and hence the concentration may be taken as practically constant during the course of the reaction. Hence the velocity equation takes the following form: $-dc_1/dt = (kc_2{}^n)c_1{}^m = k_1 c_1{}^m$, where $k_1 = k \cdot c_2{}^n$. The order of the reaction is therefore the same as m.

TABLE I.

$18 \cdot 3426$ Grams of sodium formate, $M/15$-mercuric chloride. Volume $= 150$ c.c. (where $M = $ molar).

At 25°.

$t.$	$a - x.$	k_1 (uni-molecular).
0	$16 \cdot 65$	—
48	$12 \cdot 7$	$0 \cdot 00245$
75	$11 \cdot 1$	$0 \cdot 00235$
111	$9 \cdot 5$	$0 \cdot 00220$
160	$7 \cdot 8$	$0 \cdot 00207$
Mean.........		$0 \cdot 00227$

TABLE II.

14·0362 Grams of sodium formate, $M/15$-mercuric chloride. Volume=150 c.c.

At 25°.

t.	$a-x$.	k_1.
0	16·65	—
70	12·5	0·00178
125	10·2	0·00170
168	8·8	0·00165
216	7·5	0·00160
	Mean.........	0·00168

TABLE III.

At 40°.

t.	$a-x$.	k_1.
0	16·65	—
8·5	12·4	0·0150
14·0	10·6	0·0140
20·0	9·15	0·0130
25·0	8·1	0·0125
	Mean.........	0·0136

TABLE IV.

9·1713 Grams of sodium formate, $M/15$-mercuric chloride. Volume=150 c.c.

At 25°.

t.	$a-x$.	k_1.
0	16·65	—
105	12·45	0·00120
165	10·75	0·00115
250	8·95	0·00108
310	7·85	0·00105
	Mean.........	0·00112

TABLE V.

At 40°.

t.	$a-x$.	k_1.
0	16·65	—
12·0	12·75	0·00965
22·0	10·5	0·00910
31·3	8·85	0·00877
37·5	7·9	0·00864
	Mean.........	0·00904

TABLE VI.

7·0181 Grams of sodium formate, $M/15$-mercuric chloride. Volume $= 150$ c.c.

At 25°.

$t.$	$a-x.$	$k_1.$
0	13·34	—
61	11·8	0·00087
150	9·9	0·00086
255	8·15	0·00084
550	4·9	0·00079
Mean.........		0·00084

TABLE VII.

At 40°.

$t.$	$a-x.$	$k_1.$
0	13·34	—
14	10·5	0·00743
28	8·6	0·00681
35	7·8	0·00666
56	6·0	0·00620
Mean.........		0·00677

From the foregoing Tables it will be seen that, in spite of a slight tendency to fall off, the values of k calculated for $m=1$ exhibit such a degree of constancy that the equation indicating a unimolecular reaction may fairly be regarded as the appropriate one.

Determination of n.—Supposing that k_1' and k_1'' are the values of k_1 (in the equation $k_1 = kc^n$) obtained in two experiments, in each of which the initial concentration of mercuric chloride is the same, whilst the concentrations of sodium formate are different, say, c_2' and c_2'', the following equations are obtained: $k_1' = kc_2'^n$, $k_2'' = kc_2''^n$, whence $n = \log\dfrac{k_1'}{k_1''} \Big| \log\dfrac{c_2'}{c_2''}$.

On comparing the results recorded in the foregoing tables, the following summary is obtained:—

	(1).	(2).	(3).	(4).
Grams of formate...	18·3426	14·0362	9·1713	7·0181
k_1 at 25°.	0·00227	0·00168	0·00112	0·00084

By combining these results, the actual values of n obtained are 1·12, 1·02, 1·03, 0·95, 1·0, and 1·08. It is seen that n approaches very closely to the value 1. Hence the oxidation of sodium formate by mercuric chloride is unimolecular with respect to both the reacting substances, and consequently the whole reaction is

bimolecular. The equation representing the chemical change shows it to be termolecular, and this makes it probable that the reaction takes place in stages.

In order to study the effect of change in the concentration of mercuric chloride, further experiments were made at 25°, the results of which are summarised as follows:

With 7·0181 grams of sodium formate.			With 9·1713 grams of sodium formate.		
Concentration of $HgCl_2$	$M/15$	$M/30$	Concentration of $HgCl_2$	$M/15$	$M/30$
k_1 at 25°.........	0·00084	0·00087	k_1 at 25°	0·00112	0·00116

Hence the velocity coefficients increase very slightly with the decrease in the concentration of mercuric chloride.

Temperature Coefficient of the Reaction.—From Tables II and III we get k_1 at 25°=0·00168 and k_1 at 40°=0·0136. Hence, applying van't Hoff's equation, we obtain $k_{t+10}/k_t = 4·03$. Similarly, from Tables IV and V and from VI and VII the temperature coefficient obtained is 4·02. It is rather striking that the temperature coefficient of the oxidation of sodium formate by iodine has practically the same value, namely, 4·01.

In order to determine the temperature coefficient between 40° and 50°, the following measurements were made:

TABLE VIII.

3·3805 Grams of sodium formate and $M/30$-mercuric chloride. Volume=150 c.c.

	At 40°.			At 50°.	
t.	$a-x$.	k_1.	t.	$a-x$.	k_1.
0	8·32	—	0	8·32	—
42	6·3	0·00288	10	6·55	0·0104
90	4·7	0·00276	25	4·65	0·0101
139	3·5	0·00270	39	3·45	0·0098
	Mean.........	0·000278		Mean.........	0·0101

Therefore $k_{50°}/k_{40°}=3·63$.

Applying the Arrhenius formula, we get $A=5635$ from measurements at 25° and 40°, using this value of A for the measurements at 40° and 50° we get $k_{50°}/k_{40°} = 3·61$, practically the same result as found experimentally.

The effect of manganese sulphate on the oxidation of sodium formate by mercuric chloride was studied, and the results obtained are summarised below:

TABLE IX.

9·1713 Grams of sodium formate and $M/15$-mercuric chloride. Volume = 150 c.c.

Manganese sulphate. Grams.	Mean k_1 at 25°.	Mean k_1 at 40°.	k_{t+10}/k_t.
0	0·00112	0·00903	4·02
0·0262	0·00111	0·00897	4·03
0·0524	0·00110	0·00889	4·03
1·5735	0·00098	0·00792	4·03
3·147	0·00089	0·00718	4·02
4·7205	0·00085	0·00682	4·01
6·294	0·00081	0·00643	4·0
9·441	0·00070	0·00560	4·0

Thus it appears that the greater the concentration of manganese sulphate the greater is the retardation, and the temperature coefficient in the presence of the negative catalyst is practically unchanged.

From the foregoing Tables it will be seen that, even in the presence of sodium acetate, the velocity coefficient falls off as the reaction proceeds. It was suspected that it might be due to the increase in the concentration of chloride ions. Linhart (*loc. cit.*) observed that sodium chloride retards the reaction. In order to establish this further, measurements were carried out in the presence of chlorides of several metals. Two series of measurements with zinc chloride at 25° are recorded in full in the following Tables, and these show clearly that in presence of an excess of chloride the unimolecular velocity coefficient remains more constant than that obtained when no chloride is present.

9·1713 grams of sodium formate and $M/15$-mercuric chloride were used in each case, and the volume of the mixture was 150 c.c.:

TABLE X.

With 1·096N-zinc chloride.			With 0·73N-zinc chloride.		
t.	$a-x$.	k_1.	t.	$a-x$.	k_1.
0	16·65	—	0	16·65	—
1465	13·1	0·000071	860	13·1	0·000121
2820	10·55	0·000070	1340	11·5	0·000120
3960	8·8	0·000070	2345	8·65	0·000121
4945	7·5	0·000070	3835	5·8	0·000119
Mean.........		0·000070	Mean.........		0·000120

Further experiments were made with zinc chloride as catalyst at 25° and 40° and the results obtained are summarised below:

Concentration of $ZnCl_2$	0	0·364	0·730	1·096
k_1 at 25°	0·00112	0·000276	0·000120	0 000070
Temperature coefficient.	4·02	4·16	4·32	4·46

It appears from the foregoing summary that zinc chloride produces a marked retardation in the reaction, and the greater the concentration of zinc chloride the greater is the retardation and the greater the value of the temperature coefficient.

The effects of calcium, strontium, and sodium chlorides were investigated. Instead of detailed results, the following summary is given:

TABLE XI.

9·1713 Grams of sodium formate and $M/15$-mercuric chloride. Volume = 150 c.c.:

Concentration of chloride.	Mean k_1 at 25°.	Mean k_1 at 40°.	k_{t+10}/k_t.
0	0·00112	0·00904	4·02
0·4016 N-CaCl$_2$	0·000292	0·00246	4·13
0·8032 ,,	0·000142	0·00123	4·22
1·205 ,,	0·000080	0·000732	4·38
1·6066 ,,	0·000058	0·000552	4·49
3·2134 ,,	0·000020	0·000195	4·58
0·74 N-SrCl$_2$	0·000164	0·00141	4·20
1·48 ,,	0·000076	0·000698	4·39
0·4914 N-NaCl	0·000296	0·00246	4·09
0·7234 ,,	0·000230	0·00194	4·15
0·9826 ,,	0·000163	0·00138	4·16
1·085 ,,	0·000154	0·00133	4·21
1·4466 ,,	0·000114	0·00104	4·36

Summary of results obtained with manganese chloride:

Concentration of MnCl$_2$	0	0·1722	0·4306	0·861	1·7226
k_1 at 25°.	0·00112	0·000486	0·000207	0·00008	0·000025
Temperature coefficient.	4·02	4·06	4·20	4·42 ~	4·54

All these chlorides produce a marked retarding effect; with equivalent concentrations the maximum effect is observed with zinc and manganese chlorides; both zinc and manganese ions have been found to act as retarders in the oxidation of sodium formate by mercuric chloride. The temperature coefficient is always greater the greater the retardation.

The effect of the change in the concentration of mercuric chloride was also investigated. Calcium, strontium, and sodium chlorides were used as retarders, and the concentrations of mercuric chloride were varied from $M/7·5$ to $M/50$. From the experimental results it was seen that with a given concentration of the chloride the velocity coefficient was independent of the concentration of mercuric chloride. If, however, the effect of the chloride be simply to form a complex with mercuric chloride $HgCl_2 + RCl \longrightarrow RHgCl_3$ (compare Le Blanc and Noyes, *loc. cit.*), the velocity coefficient would naturally depend on the concentrations of mercuric chloride. It was also seen that the greater the concentration of the catalyst, the greater the retardation and the greater the value of the tem-

perature coefficient. The retarding effect of chlorides on this reaction is provisionally considered to be catalytic.

It has already been said that hydrogen ions retard the oxidation of sodium formate by mercuric chloride; hence it seems probable that only formate ions are active in effecting the reduction. In order to confirm this point, a few measurements were made with pure formic acid. The experimental procedure is exactly the same as with formates; the presence of free formic acid does not interfere with the estimation of mercuric chloride by potassium iodide.

TABLE I.

0.678 N-formic acid and $M/30$-mercuric chloride.

At 25°.

t (time in minutes).	$a-x$.	k_1 (unimolecular).
0	8·3	—
4500	7·25	0·0000131
12540	6·2	0·0000101
20890	5·65	0·0000080
Mean.........		0·0000104

TABLE II.

At 40°.

t.	$a-x$.	k_1.
0	8·3	—
670	7·0	0·000110
1500	6·25	0·000082
2980	5·5	0·000060
Mean.........		0·0000840

Therefore $k_{t+10}/k_t = 4.02$.

The unimolecular velocity coefficient falls off owing to the accumulation of hydrogen chloride, which suppresses the ionisation of formic acid and at the same time forms complexes with mercuric chloride.

In order to obtain comparable results, readings were taken for times of almost equal changes in different experiments (compare Le Blanc and Noyes, *Zeitsch. physikal. Chem.*, 1890, **6**, 389). The chemical equation for the change is:

$$2HgCl_2 + H \cdot CO_2H = 2HCl + CO_2 + 2HgCl.$$
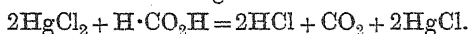
The following is a summary of the results with formic acid and mercuric chloride:

Concentration of formic acid...	0·678	1·356	2·032	4·064
k_1 at 25°	0·0000104	0·0000155	0·0000167	0·0000199
Temperature coefficient.........	4·02	4·02	3·99	4·01

It will be seen that the velocity of the reduction of mercuric chloride by formic acid is much smaller than the velocity of reduction by sodium formate of the same concentration. Moreover, the velocity coefficient does not increase proportionally with the increase in the concentration of formic acid. The electrical conductivity and freezing-point measurements of Novák (*Phil. Mag.*, 1897, [v], 46, 9) show that, by doubling the concentration of formic acid, a small increment of formate ions is produced in the solutions, and this is corroborated by kinetic measurements, which show that by doubling the concentration of formic acid we get only a small increment in the value of the velocity coefficient, and kinetic measurements also prove that only formate ions are active in the reduction; the undissociated formic acid is inactive so far as the reduction of mercuric chloride is concerned. Moreover, the temperature coefficient of this reaction is 4·02, which is exactly the same as that obtained in the reduction by formates; this shows that the processes of reduction of mercuric chloride by sodium formate and formic acid are similar in nature. On the other hand, it has been proved before that the oxidation of formic acid by chromic acid is a quadrimolecular reaction, that only undissociated formic acid is active in this reaction, and that the temperature coefficient has the value 2·07. Evidently, even with the same reducing agent, the nature of the chemical change is totally different with different oxidising agents.

Silver Nitrate and Sodium Formate.

It is well known that silver for very accurate work is usually prepared by the reduction of silver nitrate by formates, and this reaction is largely utilised in analytical chemistry. It seemed desirable to investigate the kinetics of the reaction. When silver nitrate is added to a moderately concentrated solution of sodium formate at about 25°, there is produced at first a very slight opalescence due to the formation of silver formate; then after a few seconds the silver formate begins to decompose with the separation of a black voluminous mass of metallic silver. Then, in consequence of the presence of electrolytes, the volume of the reduced silver becomes less and less, and finally a small quantity of more compact grey metallic silver is obtained.

The reduction, slow as it is, at 25° is quite measurable, even at that temperature.

Standard solutions of purified silver nitrate and sodium formate were prepared. The experimental procedure is similar to that in the oxidation of formates by mercuric chloride. After given intervals of time, measured volumes of the mixture were removed

by means of a pipette fitted with a small filtering plug and run into an excess of a standard solution of sodium chloride. The excess of chloride was then titrated by means of a standard silver nitrate solution, using potassium chromate or potassium arsenate as an indicator. In order to diminish the concentration of hydrogen ions, 2·11 grams of sodium acetate were used in each observation.

The reaction velocity may be represented by an equation of the form $-dc_1/dt = kc_1{}^m c_2{}^n$ where c_1 and c_2 represent the concentrations of silver nitrate and sodium formate respectively, and m and n the number of these molecules taking part in the reaction.

Determination of m.—In the following series of experiments, the concentration of sodium formate was much greater than that of silver nitrate, and as this does not appreciably alter during the course of the reaction, the velocity equation takes the following form:

$$-dc_1/dt = (kc_2{}^n)c_1{}^m = k_2 c_1{}^m,$$

where $k_2 = kc_2{}^n$. The order of the reaction is the same as m.

In the following Tables the amounts in c.c. of unchanged silver nitrate are recorded:

TABLE I.

3·4205 Grams of sodium formate and $N/15$-silver nitrate. Volume = 150 c.c.

At 25°.

Time in minutes.	Unchanged silver nitrate.	k_2 (bimolecular $m=2$).	k_1 (unimolecular $m=1$).
0	13·3	—	—
162	11·2	0·0000869	0·000461
449	8·75	0·0000870	0·000405
800	6·9	0·0000871	0·000356
1355	5·2	0·0000866	0·000301
	Mean.........	0·0000869	

TABLE II.

9·1713 Grams of sodium formate and $N/15$-silver nitrate. Volume = 150 c.c.

At 25°.

t.	$a-x$.	k_2 (bimolecular)
0	13·3	—
179	8·9	0·000208
365	6·6	0·000209
766	4·25	0·000208
1436	2·65	0·000210
	Mean.........	0·000209

TABLE III.

At 40°.

t.	$a-x$.	k_2.
0	13·3	—
70	7·15	0·000916
182	4·15	0·000911
303	2·85	0·000910
528	1·8	0·000910
Mean.........		0·000912

TABLE IV.

At 50°.

t.	$a-x$.	k_2.
0	13·3	—
19	8·5	0·00224
38	6·2	0·00227
64	4·55	0·00226
177	2·1	0·00227
Mean.........		0·00226

TABLE V.

16·508 Grams of sodium formate and $N/15$-silver nitrate. Volume=150 c.c.

At 25°.

t.	$a-x$.	k_2.
0	13·3	—
172	7·2	0·000370
327	5·1	0·000370
517	3·75	0·000370
1484	1·6	0·000370
Mean.........		0·000370

TABLE VI.

At 40°.

t.	$a-x$.	k_2.
0	13·3	—
32	7·9	0·00161
82	4·8	0·00162
129	3·55	0·00161
Mean.........		0·00161

TABLE VII.

At 50°.

t.	$a-x$.	k_2.
0	13·3	—
10·5	8·5	0·00404
18·5	6·65	0·00406
60·5	3·1	0·00409
Mean.........		0·00406

The values of k_2 calculated for $m = 2$ show such a degree of constancy that the equation indicating a bimolecular reaction may fairly be regarded as the appropriate one. The oxidation is evidently bimolecular with respect to silver nitrate.

Determination of n.—Supposing that k_2' and k_2'' are the values of k_2 obtained in two experiments, in each of which the initial concentration of silver nitrate is the same, whilst the concentrations of sodium formate are different, say c_2' and c_2'', the following equations are obtained: $k_2' = kc_2'^n$, $k_2'' = kc_2''^n$, whence

$$n = \log \frac{k_2'}{k_2''} \bigg/ \log \frac{c_2'}{c_2''}.$$

On comparing the foregoing measurements recorded at 25°, the following summary is obtained:

	(1).	(2).	(3).
Grams of formate......	16·508	9·1713	3·4205
k_2 at 25°.................	0·000370	0·000209	0·0000868

By combining these results, the values of n actually obtained are 1·09, 0·96, and 0·90. It is seen n approaches closely to the value 1, and consequently 1 molecule of sodium formate takes part in the reaction. The whole reaction is, therefore, termolecular, bimolecular with respect to silver nitrate, and unimolecular with regard to sodium formate (compare Noyes and Cottle, *Zeitsch. physikal. Chem.*, 1898, **27**, 579).

In order to study the change in the concentration of silver nitrate on the velocity coefficient of this reaction, further measurements were made at 25°, and the results obtained are summarised below:

With 9·1713 grams of sodium formate:

Concentration of $AgNO_3$ ...	$N/15$	$N/30$	$N/50$
k_2 at 25°	0·000209	0·000212	0·000210

With 16·508 grams of sodium formate:

Concentration of $AgNO_3$ ...	$N/15$	$N/30$
k_2 at 25°	0·000370	0·000372

With 3·4205 grams of sodium formate:

Concentration of $AgNO_3$ ...	$N/15$	$N/30$
k_2 at 25°	0·0000869	0·0000870

Evidently change in the concentration of silver nitrate has practically no influence on the velocity coefficients, hence there is no disturbing factor, and the reaction is truly termolecular.

The chemical equation for this reaction is:

$$2AgNO_3 + H \cdot CO_2Na = HNO_3 + NaNO_3 + CO_2 + 2Ag.$$

Hence the reaction is simple and does not take place in stages.

Temperature Coefficient.—From Tables II, III, and IV we get k_2 at 25° = 0·000209, k_2 at 40° = 0·000912, and k_2 at 50° = 0·00226. Hence by applying van't Hoff's formula we get k_{t+10}/k_t between 25° and 40° = 2·67, and between 40° and 50° = 2·48.

If the Arrhenius formula is used, the following results are obtained:

t.	k_2 (obs.).	k_2 (calc.).
25°	0·000209	(0·000209)
40°	0·000912	(0·000912)
50°	0·00226	0·00226

$$A = 3977.$$

It has been previously shown that the temperature coefficient of the oxidation of sodium formate by iodine and mercuric chloride has the value 4·02 between 25° and 40°, and both these reactions are bimolecular. Although the oxidation of sodium formate by silver nitrate is a much slower reaction than the other two, the temperature coefficient is much lower than those in the other cases. Evidently there seems to be a connexion between the order of a reaction and its temperature coefficient. From this investigation it will be clear that under similar conditions iodine is a better oxidising agent than mercuric chloride and the latter is a much better oxidising agent than silver nitrate. Evidently from kinetic measurements, under exactly similar conditions, we can compare the relative oxidising or reducing property of substances quite accurately.

The effect of a manganese salt was studied.

The results obtained with manganese sulphate as catalyst are summarised below:

9·1713 Grams of sodium formate and $N/15$-silver nitrate. Volume $=150$ c.c.

Manganese sulphate. Grams.	Mean k_2 at 25°.	Mean k_2 at 40°.	Temperature coefficient.
0	0·000209	0·000912	2·67
0·0524	0·000207	0·000905	2·67
1·5735	0·000187	0·000811	2·66
3·147	0·000170	0·000740	2·66
6·294	0·000142	0·000621	2·67
12·588	0·000109	0·000475	2·66

From the above figures it appears that manganese sulphate is a negative catalyst in the oxidation of sodium formate by silver nitrate. The greater the concentration of the catalyst, the greater is the retardation. This reaction, like the oxidation of sodium formate by mercuric chloride, is not so sensitive to the influence of traces of manganese sulphate as the oxidation of formic acid by chromic acid previously studied. Moreover, the temperature coefficient is the same as that obtained without any manganese sulphate.

Mechanism of Chemical Change and Temperature-Coefficient.

It is well known that temperature has a marked influence on the velocity of reactions, the average value of the temperature-coefficient being about 2·5 for a rise of 10° in the case of non-actinic chemical changes. This exponential increase of velocity with temperature cannot be explained from the mere increase in kinetic movement, for this should mean an increase of only about 2 per cent. in the velocity of the reaction for the same change of temperature. It is clear, therefore, that the temperature effect must be due to some influence connected with the internal structure of the molecules taking part in the reaction.

The phenomena of ordinary positive catalysis as well as photochemical catalysis in homogeneous medium have made us familiar with the acceleration of reactions at constant temperature, and this must similarly be due to some effect connected with the structure of the molecules.

It seems, therefore, probable that the effects of increase of temperature, of light, and of chemical catalysts in a reaction are intimately connected and are possibly identical in nature.

As was first suggested by Arrhenius (*Zeitsch. physikal. Chem.*, 1889, **4**, 226), the effect of temperature has been ascribed to the existence of an equilibrium between so-called "active" and "inactive" molecules, such equilibrium being sensitive to changes of

temperature; and hence a rise of temperature by bringing into existence more "active" molecules causes a reaction velocity very much in excess of what one would expect on a merely kinetic view.

Arrhenius has even deduced an expression $d \log k / dT = A / T^2$, showing the effect of temperature in terms of a quantity A, which on this view is taken to be half the energy change involved in the transformation of one molecule of "inactive" to "active."

If such "active" and "inactive" molecules exist, it appears reasonable to expect that a catalyst or light simply acts in shifting this equilibrium. Plainly if sufficient catalyst were added to change a relatively large amount of "inactive" to "active" molecules or *vice versâ*, it would follow that, when the catalyst is present in large quantities, the temperature coefficient should be smaller (in the case of positive catalysis) and greater (in the case of negative catalysis) than that observed when the reaction is not catalysed or only feebly so. For when much catalyst is present, the transformation from "inactive" to "active" in the case of positive catalysis would have already taken place, and therefore temperature should have less additional accelerating effect; the reverse would be the case in negative catalysis. This hypothesis can be tested by the experiments with chemical catalysts already recorded in this paper.

In order to apply the hypothesis to photochemical catalysis, the following investigations were carried out. Goldberg (*Zeitsch. physikal. Chem.*, 1902, **41**, 1; *Zeitsch. wiss. Photochem.*, 1906, **4**, 61), who studied the oxidation of quinine sulphate by chromic acid in light, found the temperature coefficient of the reaction to be 1·04 for a 10° rise in temperature. The temperature coefficient of this reaction in the dark has been determined by the author as described below.

In order to exclude light, "resistance" glass bottles were thoroughly covered with a thick coating of "club black enamel." This enamel can withstand hot water fairly well, and light is completely excluded by a thick coating. The chromic acid, which remained unchanged, was estimated by iodometric measurement with standard thiosulphate.

Quinine and Chromic Acid.

TABLE I.

1·322 Grams of quinine sulphate, $N/85$-chromic acid, and $30N/17$-sulphuric acid. Volume = 85 c.c.

At 25°.

t.	$a-x$.	k_1 (uni-molecular).
0	8·15	—
450	7·0	0·000150
1420	4·95	0·000152
3210	2·6	0·000154
	Mean......	0·000152

TABLE II.

At 60°.

t.	$a-x$.	k_1.
0	8·12	—
101	5·9	0·00137
187	4·5	0·00137
290	3·2	0·00139
	Mean......	0·00138

Therefore temperature coefficient between 25° and 60° $= k_{t+10}/k_t = 1·88$.

TABLE III.

1·322 Grams of quinine sulphate, $N/85$-chromic acid, and $60N/17$-sulphuric acid. Volume = 85 c.c.

At 25°.

t.	$a-x$.	k_1.
0	8·15	—
258	6·9	0·000281
540	5·75	0·000280
1590	2·9	0·000282
	Mean......	0·000281

TABLE IV.

At 60°.

t.	$a-x$.	k_1.
0	8·12	—
43·5	6·3	0·00254
67	5·5	0·00252
100	4·5	0·00255
150	3·37	0·00254
	Mean......	0·00254

Therefore k_{t+10}/k_t between 25° and 60° = 1·87.

Sulphuric acid only accelerates the reaction and was used by Goldberg in his work. The reaction, carried on in the dark, has a higher value (1·87) for its temperature coefficient than that in the light (1·04) under similar conditions. Thus the acceleration caused by the positive catalyst (light) produces a marked lowering of the temperature coefficient.

Iodine and Potassium Oxalate.

In a former paper (Dhar, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1097) it was found that the oxidation of oxalates by iodine was very sensitive to light; light acted here as a strong positive catalyst. This reaction was investigated in diffused daylight and in the dark. The reaction in the case of potassium oxalate may be represented by the equation

$$K_2C_2O_4 + I_2 \longrightarrow 2KI + 2CO_2.$$
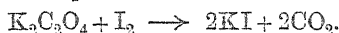
As in the case of the formate oxidation, sublimed iodine was used and the potassium oxalate was purified by several recrystallisations and carefully dried centrifugally. The solution of oxalate was standardised by precipitating a known volume as calcium oxalate, igniting in a platinum crucible, and weighing as lime.

From time to time the unchanged iodine was estimated by means of standard sodium thiosulphate.

The velocity of the reaction may be represented by an equation of the form $-dc_1/dt = kc_1{}^m c_2{}^n$, where c_1 and c_2 represent concentrations of iodine and oxalate respectively.

Determination of m.—In the following series of experiments the oxalate used was in large excess, and hence the concentration might be supposed to be practically constant during the course of the reaction; hence the velocity equation takes the following form:

$$-dc_1/dt = (kc_2{}^n)c_1{}^m = k_1 c_1{}^m,$$

where $k_1 = kc_2{}^n$. The order of the reaction is the same as m.

Measurements in the Dark at 50°.

TABLE V.

18·7080 Grams of potassium oxalate, 0·1677 gram of iodine, and 0·8476 gram of potassium iodide. Volume = 150 c.c.

t.	$a - x$.	k_1 (unimolecular).
0	14·37	—
90	9·24	0·00213
155	6·6	0·00218
220	4·7	0·00220
280	3·4	0·00223
	Mean......	0·00218

TABLE VI.

9·354 Grams of potassium oxalate, 0·1677 gram of iodine, and 0·8476 gram of potassium iodide. Volume = 150 c.c.

t.	$a-x$.	k_1.
0	14·37	—
100	11·5	0·000967
260	8·0	0·000978
485	4·8	0·000981
	Mean......	0·000975

TABLE VII.

4·6770 Grams of potassium oxalate, 0·1677 gram of iodine, and 0·8476 gram of potassium iodide. Volume = 150 c.c.

t.	$a-x$.	k_1.
0	14·37	—
245	11·2	0·000442
500	8·5	0·000456
725	6·6	0·000466
	Mean......	0·000455

From the foregoing Tables, it will be seen that the values of k calculated for $m = 1$ exhibit such a degree of constancy that the equation indicating a unimolecular reaction may fairly be regarded as the appropriate one.

Determination of n.—Supposing that k'_1 and k''_2 are the values of k_1 (in the equation $k_1 = kc^n$) obtained in two experiments, in each of which the initial concentration of iodine is the same, whilst the concentrations of potassium oxalate are different, say c_2' and c_2'', the following equations are obtained:

$$k_1' = kc_2'^n,\ k_1'' = kc_2''^n\ ;\ \text{whence } n = \log\frac{k_1'}{k_1''} \bigg| \log\frac{c_1'}{c_2''}.$$

From the measurements recorded in the foregoing Tables, the following summary of results is obtained:

	(1).	(2).	(3).	
				0·1677 gram of iodine and 0·8476
Grams of oxalate	18·7080	9·354	4·677	gram of potassium
Value of k at 50°	0·00217	0·000975	0·000455	iodide.

Combining these results, the values of n actually obtained are 1·1, 1·1, and 1·09.

It is seen that n approaches very closely to the value 1. These results show that the oxidation of potassium oxalate by iodine is unimolecular with respect to both iodine and potassium oxalate, and consequently the whole reaction is bimolecular; this is quite

in accordance with the equation representing the chemical change.

In order to determine the temperature coefficient of the reaction in the dark, measurements were made at different temperatures.

TABLE VIII.

18·7080 Grams of potassium oxalate, 0·1677 gram of iodine, and 0·8476 gram of potassium iodide.   Volume = 150 c.c.

At 25°.

t.	$a-x$.	k_1.
0	14·37	—
7,015	10·8	0·0000177
12,835	8·4	0·0000181
24,000	4·95	0·0000193
	Mean......	0·0000184

TABLE IX.				TABLE X.		
At 40°.				At 60°.		
t.	$a-x$.	k_1.		t.	$a-x$.	k_1.
0	14·37	—		0	14·37	—
265	11·65	0·000343		14	10·0	0·0113
520	9·35	0·000358		31	6·25	0·0119
1270	4·9	0·000367		47	3·9	0·0121
	Mean......	0·000356			Mean......	0·0118

Summary of Results.

18·708 grams of potassium oxalate, 0·1677 gram of iodine, and 0·8476 gram of potassium iodide

Temperature	25°	40°	50°	60°
k_1	0·0000184	0·000356	0·00218	0·0118

Hence k_{t+10}/k_t between 25° and 40° = 7·2, between 40° and 50° = 6·1, and between 50° and 60° = 5·4.   It is seen that the temperature coefficient of the oxidation of oxalates by iodine in the dark is quite large and is 7·2 between 25° and 40°, and falls off with increase of temperature.

Applying the Arrhenius formula $\log k_1/k_2 = A(T_1 - T_2)/T_1T_2$, the following results are obtained; $A = 7989$:

Temperature.	k (found).	k (calc.).
25°	0·0000184	(0·0000184)
40°	0·000356	(0·000356)
50°	0·00218	0·00219
60°	0·0118	0·0121

The same reaction was studied in diffused daylight. The reaction velocity was greater in diffused daylight than in the dark.

In Diffused Daylight at 50°.

TABLE XIII.

18·7080 Grams of potassium oxalate, 0·254 gram of iodine, and 1·0826 grams of potassium iodide. Volume=150 c.c.

t.	$a-x$.	k_1 (unimolecular).
0	19·7	—
65	13·8	0·00238
170	7·75	0·00238
315	3·4	0·00242
	Mean......	0·00239

TABLE XIV.

9·354 Grams of potassium oxalate, 0·254 gram of iodine, and 1·0826 grams of potassium iodide. Volume=150 c.c.

t.	$a-x$.	k_1 (unimolecular).
0	19·7	—
90	15·8	0·00106
210	11·85	0·00105
341	8·85	0·00102
480	6·4	0·00102
	Mean......	0·00104

TABLE XV.

4·677 Grams of potassium oxalate, 0·254 gram of iodine, and 1·0826 grams of potassium iodide. Volume=150 c.c.

t.	$a-x$.	k_1.
0	19·7	—
120	16·9	0·000555
240	14·6	0·000542
360	12·7	0·000530
480	11·0	0·000527
	Mean......	0·000539

Summary of Results.

			(1).	(2).	(3).
0·254 gram of iodine and 1·0826 grams of potassium iodide	{	Grams of potassium oxalate	18·708	9·354	4·677
	{	k_1 at 50°	0·00239	0·00104	0·000539

Combining these results, the values of n actually obtained are 1·2, 1·07, and 0·90. Hence it is seen that n approaches unity. Consequently the reaction is unimolecular with respect to both iodine and oxalate, and the order of the reaction is not altered in diffused light.

In order to determine the temperature coefficient in diffused daylight, measurements were made at 25°.

TABLE XVI.

18·708 grams of potassium oxalate, 0·254 gram of iodine, and 1·0826 grams of potassium iodide.   Volume = 150 c.c.

t.	$a-x$.	k_1.
0	19·7	—
360	17·9	0·000114
1440	13·55	0·000113
2880	9·5	0·000110
Mean		0·000112

TABLE XVII.

4·677 grams of potassium oxalate, 0·2295 gram of iodine, and 0·6492 gram of potassium iodide.   Volume = 150 c.c.

t.	$a-x$.	k_1.
0	19·66	—
480	18·9	0·0000356
1440	17·45	0·0000359
11000	8·0	0·0000355
Mean		0·0000357

Summary of Results.

		A.	
18·7080 grams of potassium oxalate, 0·254 gram of iodine, and 1·0826 grams of potassium iodide	Temperature	25°	50°
	Value of k_1	0·000112	0·00239
		B.	
4·677 grams of potassium oxalate, 0·2295 gram of iodine, and 0·6492 gram of potassium iodide	Temperature	25°	50°
	Value of k_1	0·0000357	0·000741

From A :

Temperature coefficient between 25° and 50° = 3·40. and from B :

$$k_{t+10}/k_t \text{ between } 25° \text{ and } 50° = 3·36.$$

The temperature coefficient between 25° and 50° of the oxidation of potassium oxalate by iodine in the dark has the value 6·73; whilst in diffused light it is 3·4.

Evidently the acceleration of the oxidation of potassium oxalate by iodine in diffused daylight produces a lowering in the value of the temperature coefficient.

Mercuric Chloride and Potassium Oxalate.

It is well known that a mixture of an oxalate and mercuric chloride has been utilised as an actinometer. Eder (*Sitzungsber. K. Akad. wiss. Wien*, October, 1879) has made a thorough study of this actinometer and has measured the amount of mercurous

chloride obtained at various temperatures in the presence of light. His results show that the temperature coefficient for a 10° rise between 0° and 80° is 1·19.

In the present investigation the velocity of this reaction at different temperatures in the dark was studied. The reaction being slow, measurements were made at 79·6° and 99·6° with glycerol as the thermostat liquid.

Since preliminary experiments showed that carbon dioxide, which is a product of the chemical reaction, markedly accelerates the change. Both the reacting substances were saturated with carbon dioxide before mixing. As in the case of the oxidation of formates by mercuric chloride, definite volumes of the mixture were withdrawn from time to time by means of a pipette fitted with a plug of cotton-wool, and added to an excess of potassium iodide. The excess of potassium iodide was titrated against a standard solution of mercuric chloride.

In the Dark.

TABLE I.

At 99·6°.

31·430 Grams of potassium oxalate and $M/15$-mercuric chloride. Volume = 150 c.c.

t.	$a-x$.	k_1 (unimolecular).
0	13·3	—
58	9·4	0·00260
140	5·75	0·00260
270	2·6	0·00262
	Mean	0·00261

TABLE II.

At 99·6°.

15·715 Grams of potassium oxalate and $M/15$-mercuric chloride. Volume = 150 c.c.

	$a-x$.	k_1.
0	13·3	—
142	8·7	0·00130
280	5·75	0·00130
418	3·7	0·00133
	Mean	0·00131

TABLE III.

At 99·6°.

7·8575 Grams of potassium oxalate and $M/15$-mercuric chloride.
Volume = 150 c.c.

$t.$	$a-x.$	$k_1.$
0	13·3	—
343	8·0	0·000643
535	6·0	0·000646
1060	2·7	0·000653
	Mean	0·000647

TABLE IV.

At 79·6°.

31·430 Grams of potassium oxalate and $M/15$-mercuric chloride.
Volume = 150 c.c.

$t.$	$a-x.$	$k_1.$
0	13·3	—
415	8·1	0·00052
610	6·5	0·00051
925	4·3	0·00053
	Mean	0·00052

TABLE V.

At 79·6°.

15·765 Grams of potassium oxalate and $M/15$-mercuric chloride.
Volume = 150 c.c.

$t.$	$a-x.$	$k_1.$
0	13·3	—
570	2·45	0·00026
1380	5·65	0·00027
1680	4·5	0·00028
	Mean	0·00027

TABLE VI.

At 79·6°.

7·8575 Grams of potassium oxalate and $M/15$-mercuric chloride.
Volume = 150 c.c.

$t.$	$a-x.$	$k_1.$
0	13·3	—
1124	9·5	0·00013
1555	8·35	0·00013
2630	5·7	0·00014
	Mean	0·000133

From the foregoing Tables it will be seen that, in spite of a slight tendency to rise, the values of k calculated for $m = 1$ exhibit such a degree of constancy that the equation indicating a unimolecular reaction may fairly be regarded as the appropriate one.

Determination of n.—Supposing that k_1' and k_1'' are the values of k_1 (in the equation $k_1 = kc^n$) obtained in two experiments, in each of which the initial concentration of mercuric chloride is the same, whilst the concentrations of potassium oxalate are different, say c_2' and c_2'', the following equations are obtained:

$$k_1' = kc_2'^n, kc_1'' = kc_2''^n; \text{ whence } n = \log \frac{k_1'}{k_1''} \Big| \log \frac{c_2'}{c_2''}.$$

The measurements recorded in the foregoing Tables may, therefore, be employed in determining the value of n.

On comparing, the following summary of results is obtained:

At 99·6°.

	(1).	(2).	(3).
Grams of oxalate	30·430	15·715	7·8575
Value of k_1	0·00261	0·00131	0·000647

Combining these results, the values of n actually obtained are 1, 1·06, 1·02. It is seen that n approaches very closely to the value 1. Consequently the oxidation of potassium oxalate by mercuric chloride is unimolecular with respect to both the reacting substances, that is, the whole reaction is bimolecular, although the chemical equation shows it to be termolecular:

$$2HgCl_2 + K_2C_2O_4 = 2HgCl + 2KCl + 2CO_2.$$
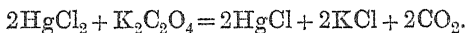
The reaction probably takes place in stages.

From Table I we get k_1 at $99·6° = 0·00261$ and from Table IV k_1 at $79·6° = 0·00052$; therefore by van't Hoff's equation we get $k_{t+10}/k_t = 2·24$. Similarly from Tables II and V, also from III and VI, the temperature coefficients obtained are 2·20 and 2·21. Hence it is seen that the temperature coefficient of the oxidation of potassium oxalate by mercuric chloride in the dark is 2·2, whilst in light it is 1·19. Light acting as an accelerator produces a concomitant reduction in the temperature coefficient.

There are a few cases on record where reactions have been investigated both in the light and in the dark.

Brunner and Dluska (*Bull. Acad. Sci. Cracow*, 1907, 707) have studied the bromination of toluene and found the temperature coefficient in light to be equal to 1·8, whilst in the dark it is 4·5.

Plotnikov (*Zeitsch. physikal. Chem.*, 1907, **58**, 64, 214; 1911, **75**, 385) also investigated two reactions and found the following values:

Oxidation of Hydrogen Iodide by Oxygen.

	In the light.	In the dark.
Temperature coefficient for 10° rise	1·4	2·86

Action of Oxygen on Iodoform dissolved in Benzene or Alcohol.

	In the light.	In the dark.
Temperature coefficient for 10° rise	1·42	2·61

In all these cases light acts as a positive catalyst and markedly accelerates the reactions. Evidently when there is acceleration produced by light we have a concomitant lowering of the temperature coefficient, and the greater the acceleration the greater will be the lowering of the temperature coefficient of the light reaction.

In reactions in which the velocity is greatly accelerated by light we expect the value of the temperature coefficient to be about 1·04 to 1·39; but when light acts as a negative catalyst we should expect an increase in the value of its temperature coefficient.

As a matter of fact, Trautz (*Physikal. Zeitsch.*, 1906, **7**, 899) has shown that the oxidation of sodium sulphide and of pyrogallol by oxygen are retarded by violet light, and he has found the temperature coefficients to be 3·5 in the case of sodium sulphide and 2·4 in the case of pyrogallol. These temperature coefficients are much larger than those for photochemical reactions, in which light is an accelerator.

Slator (*Zeitsch. physikal. Chem.*, 1903, **45**, 513) investigated the chlorination of benzene in the presence of several chemical catalysts and of light. The reaction velocity in absence of any catalyst is very small. Of the three positive catalysts used in this reaction, iodine chloride, stannic chloride, and ferric chloride, the first was found to be the most effective, then stannic chloride, and lastly ferric chloride. The temperature coefficients in the presence of these catalysts are as follows:

Catalyst	ICl	$SnCl_4$	$FeCl_3$
Temperature coefficient $= k_{t+10}/k_t$	1·05	1·5	2·5

Light also accelerates the reaction, and the temperature coefficient in the presence of light is 1·5. It is clear that the greater the acceleration produced by a given catalyst, the smaller is the value of the temperature coefficient; the temperature coefficient of the reaction with the strong positive catalyst, iodine chloride, in the dark is much smaller than that of the reaction carried on in the light without any chemical catalyst. A strongly catalysed reaction in the dark may have a very small temperature

coefficient, just like a photochemical reaction. This is in harmony with the hypothesis.

Recent work of Padoa (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 168, 215) has brought further evidence in favour of the hypothesis in question. He has studied the temperature coefficients of the action of monochromatic light on chlorine–hydrogen mixtures, on a photographic plate, and on some phototropic transformations. With the chlorine–hydrogen mixture the following temperature coefficients were obtained:

White light, 1·29; green ($\lambda = 550$—530 $\mu\mu$), 1·50; blue ($\lambda = 490$—470 $\mu\mu$), 1·31; violet ($\lambda = 460$—440), 1·21; ultra-violet ($\lambda = 400$—350), 1·17.

Thus the value of the temperature coefficient increases with the wave-length of light. The chemical activity of these rays increases with the decrease of the wave-length.

Exactly similar results have been obtained with the photographic plate and the phototropic transformations; the greater the intensity (and hence the acceleration), the smaller is the temperature coefficient.

From a consideration of the experimental verification of this hypothesis in the case of chemical catalysts, it is found that sulphuric acid markedly accelerates the oxidation of formic acid by chromic acid, and in this case the accelerating effect increases more rapidly than the accelerator, and if the concentrations of sulphuric acid are plotted as abscissæ, and the corresponding velocity coefficients as ordinates, an exponential curve is obtained (compare Rosanoff, *J. Amer. Chem. Soc.*, 1913, **35**, 173). According to this hypothesis, the temperature coefficient in the presence of sulphuric acid should be less than that in the absence of the catalyst. As a matter of fact, all the experimental work with sulphuric acid recorded in the foregoing pages supports this deduction. Here only one typical case is cited:

3·0833 N-formic acid and N/30-chromic acid	Concentration of H_2SO_4	0	N/6	N/3	$2N$/3
	k_{t+10}/k_t between 25° and 50°	2·03	1·87	1·86	1·84

Hence we find that the greater the concentration of sulphuric acid, the greater is the fall in the temperature coefficient.

On the other hand, manganese chloride is a negative catalyst in the oxidation of formic acid by chromic acid, and it has been proved that in the presence of this salt the temperature coefficient is appreciably higher than that in the absence of the catalyst.

The oxidation of oxalic acid by chromic acid is retarded in the

presence of an excess of sulphuric acid, and the following results are obtained for the temperature coefficient:

N/20-oxalic acid and N/100-chromic acid $\begin{cases} \text{Concentration of } H_2SO_4 & 0 \quad 3N/5 \quad 8N/5 \quad 4/N \\ k_{t+10}/k_t \text{ between } 25° \\ \quad \text{and } 40° \text{ .... } 1.96 \quad 2.18 \quad 2.32 \quad 2.66 \end{cases}$

Thus sulphuric acid, acting as a negative catalyst, produces an increase in the temperature coefficient. Similarly in this oxidation boric acid, molybdic acid, and ammonium molybdate are retarders, and in their presence the temperature coefficient is higher than in their absence.

In the oxidation of sodium formate by mercuric chloride, it has been found that chlorides are retarders, and in their presence the temperature coefficient is appreciably increased. By considering the case of manganese chloride:

Concentration of $MnCl_2$...	0	0.1722	0.4306	0.8613	1.7726
k at 25°	0.00112	0.000486	0.000207	0.000081	0.000025
Temperature coefficient...	4.02	4.06	4.2	4.42	4.54

one finds the retarding effect increasing more rapidly than the retarder. Exactly similar results are obtained with zinc chloride.

In the oxidation of sodium formate by silver nitrate, zinc and calcium nitrates have been found to be great retarders, and in their presence the temperature coefficient is higher than that determined in their absence.

In the oxidation of sodium formate by iodine, potassium iodide is a retarder; the temperature coefficient does not practically change in the presence of potassium iodide. This is due, probably, to the following reason. From the work of Taylor (*Proc. Roy. Soc. Edin.*, 1905, **25**, 231; 1908, **28**, 461) on the viscosity of aqueous solutions the following results are obtained:

Temperature.	Viscosity of N-potassium iodide.	Viscosity of water.
0°	0.854	1.000
15°	0.583	0.640
25°	0.467	0.501

The ratio of the viscosity of water at 25° and 15° = 0.793, whilst that of N-potassium iodide is 0.801. It is well known that the greater the viscosity, the smaller is the velocity coefficient of a reaction. Evidently in the presence of potassium iodide the ratio of the velocity coefficients at 25° and 15°, that is, the temperature coefficient, would be smaller than that obtained in water. This effect is more pronounced with more concentrated potassium iodide solutions. In the presence of a large excess of potassium iodide, the experimental results show that the tempera-

ture coefficient, instead of being higher, is actually lower than the value obtained with very dilute solutions. In these cases the changes in viscosity more than counterbalance the effect due to the change of "active" molecules into the "inactive" state.

Lewis (T., 1914, **105**, 2330; 1915, **107**, 233; 1916, **109**, 796) has studied the hydrolysis of methyl acetate and sucrose in the presence of different concentrations of hydrochloric acid at different temperatures, but in both these cases the difference obtained in the temperature coefficients of a feebly and a strongly catalysed reaction is very small. His results may be explained in the light of the viscosity changes already indicated.

On the other hand, the work of Clark (*J. physical Chem.*, 1907, **11**, 353), who has studied the accelerating effect of chromic acid on the interaction of bromic and hydriodic acids, and of Müller (*Bull. Soc. Chim.*, 1911, [iv], **9**, 185) on the accelerating effect of hydrochloric acid on the action of iodine on sodium dithionate, shows that the temperature coefficient falls off with the increase in the concentration of the catalysts.

Moreover, Holmberg (*Zeitsch. physikal. Chem.*, 1912, **79**, 146) has studied the action of hydroxides of the alkali and alkaline earth metals on the hydrolysis of dibromosuccinic acid, and has found that the greater the acceleration the smaller is the temperature coefficient. The work of de Bruyn and Sluiter (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, **6**, 773) on the transformation of acetophenoneoxime into acetanilide is also in favour of the hypothesis.

This is practically all the literature that is available at present to test this hypothesis. In spite of the fact that numerous catalytic reactions have been investigated, an examination of the literature has shown that in very few cases have catalyst and temperature been varied simultaneously.

In studying the kinetics of the reactions described in this paper the "isolation method" of Ostwald was always used. In the investigation of multimolecular reactions this method has several advantages. By increasing the concentration of one of the reacting substances we can increase the speed so as to bring the reaction within the range of convenient experimental conditions. The oxidation of formic acid by chromic acid is a case in point. The study of the kinetics of the reaction is only possible by having an excess of formic acid; otherwise the reaction is too slow to measure its velocity.

Moreover, by having an excess of one of the reacting substances, the concentration of that reactant does not enter into the question of the velocity, and hence the kinetics become much simpler.

Although the action of chromic acid on formic acid is a quadri-molecular reaction, in the presence of an excess of the latter acid the reaction follows the unimolecular formula and becomes quite easy to investigate.

In order to study the effect of dilution on temperature-coefficients, the concentrations of the reacting substances have been widely varied. In the formic acid oxidation, temperature coefficients have been determined using different concentrations of formic acid with a definite concentration of chromic acid. Although, by the change in the concentration of formic acid, the velocity coefficients have widely different values, the temperature coefficients remained practically the same in all cases. Exactly similar results were obtained in the other reactions investigated in this paper. Evidently dilution has no appreciable effect on the equilibrium between "active" and "inactive" molecules. In an important paper Halban (*Zeitsch. physikal. Chem.*, 1909, **67**, 176) has shown that unimolecular reactions have larger temperature coefficients than those of multimolecular ones. In addition to the cases enumerated by him, the following are a few more examples in favour of this view. The temperature coefficient of the intra-molecular change of acetobromoamide has the value 5·37 between 16° and 25° (van Dam, *Rec. trav. chim.*, 1900, **19**, 318), and Kremann (*Monatsh.*, 1910, **31**, 245, 1051) has shown that the temperature coefficient of the velocity of decomposition of ethyl hydrogen sulphate in water has the value 4·5 between 55° and 65°. Also Rivett (*Zeitsch. physikal. Chem.*, 1913, **82**, 201) has obtained 3·27 for the temperature coefficient of the change of acetochloroanilide to *p*-chloroacetanilide. Halban's view that reactions which are really multimolecular, but owing to the presence of one of the ingredients in excess appear to be unimolecular, have higher temperature coefficients seems doubtful

In this investigation it has been shown that the oxidations of formic and oxalic acids by chromic acid follow the unimolecular formula when an excess of formic or oxalic acid is present. Although the reactions are unimolecular, the temperature coefficients are not high, the values being 2·03 for formic acid and 1·94 for oxalic acid between the temperature interval of 25° and 40°. It has already been stated that change in the concentration of formic acid, for example, has no effect on the temperature coefficient. By increasing the concentration of one of the reactants, a bimolecular reaction can be made to appear as a unimolecular one; according to Halban's view, the same reaction will have a temperature coefficient in the unimolecular condition different from that in the bimolecular state. This is not

corroborated by experiments. As a matter of fact, the oxidation of potassium oxalate by iodine in the dark is a bimolecular reaction, and has the temperature coefficient 7·2 between 25° and 40°. Similarly, the bimolecular reactions—the oxidation of sodium formate by iodine and by mercuric chloride—have a temperature coefficient of 4·02. It appears, therefore, that the temperature coefficients of both bi- and uni-molecular reactions can be higher than those of multimolecular reactions.

In a similar way Hirniak's work (*Chem. Zentr.*, 1914, i, 3) on the temperature coefficients of the reaction between dimethylaniline and ethyl iodide can be easily explained. In this investigation it has been shown that under exactly similar conditions the oxidation of oxalic acid by chromic acid has a greater velocity and smaller temperature coefficient than those of the oxidation of formic acid by chromic acid. Similar results have been obtained by Kremann (*loc. cit.*) and Hirniak (*loc. cit.*). From their work it can be seen that, when the order of the reactions considered is the same, those with greater velocities have smaller temperature coefficients. All these facts, and the deduction of Skrabal *Monatsh.*, 1914, **35**, 1157; 1916, **37**, 191) that immeasurably rapid reactions have a temperature coefficient of unity, can be easily understood on the basis of the hypothesis of "active" and "inactive" molecules, since an immeasurably rapid reaction is possible when the number of "active" molecules are very large, and this being the case, temperature will have very little effect on this reaction.

Recently a purely physical concept of active molecules has been introduced by Marcelin (*Compt. rend.*, 1914, **158**, 161) and Rice (*Brit. Assoc. Report*, 1915, 397). By treating the problem of reaction velocity from the point of view of statistical mechanics, they have correlated the reaction velocity with the temperature on the assumption that only those molecules react which reach a "critical" condition, in which they acquire a certain energy considerably in excess of the average energy per molecule of the system.

Rice's equation is

$$\frac{d \log k}{dT} = \frac{Vc - Vm + \frac{1}{2}RT}{RT^2},$$

where Vm is the mean potential energy of the molecular group in question, so that $Vc - Vm$ is the "critical" increment of energy necessary for the reaction.

The forces involved are supposed to be electromagnetic, and therefore subject to modification due to change of radiation density produced by a catalyst. This leads to the conclusion that

a positive catalyst, by reducing $Vc - Vm$, increases k, but decreases $d \log k/dT$, and vice versâ for a negative catalyst. These deductions are in agreement with the experimental results brought forward in this paper.

Furthermore, in a recent experimental paper on the photochemical changes occurring in aqueous solutions of chloroplatinic acids, Boll (*Ann. Physique*, 1914, [ix], **2**, 5, 226) has concluded from his work that there exist intermediate active phases of the reacting molecules. Goldschmidt (*Physikal. Zeitsch.*, 1909, **10**, 206, 421), from theoretical considerations, also draws a similar conclusion. Moreover, the recent work by Baly and his pupils (T., 1908, **93**, 2108; 1912, **101**, 1469, 1475) on the absorption spectra of compounds has experimentally proved the existence of those very active phases of molecules as intermediate stages in chemical reactions such as advocated in this paper.

LXIII.—*A Synthesis of Tropinone.*

By ROBERT ROBINSON.

AMONG the noteworthy achievements of Willstätter in connexion with his investigation of the chemistry of tropine, there was nothing that contributed a greater share to the final solution of the problems encountered than the demonstration of the constitution of tropinone, a ketone first produced in 1896 (Willstätter, *Ber.*, 1896, **29**, 396; Ciamician and Silber, *ibid.*, 490) by the oxidation of tropine, and later by a similar method from ecgonine (Willstätter, *Ber.*, 1898, **31**, 2655). This substance has become the central figure in the atropine group of the alkaloids, and, as shown below, may be regarded as the natural starting point in the synthetical preparation of a number of bases of great value in the practice of medicine and surgery.

Tropine $\xleftarrow[\text{reduction}]{\text{electrolytic}}$ Tropinone $\xrightarrow[\text{CO}_2]{\text{Na}}$ Tropinonecarboxylic acid

Tropoylation — mandelorylation ↘

benzoylation / Na and $C_5H_{11}OH$

Atropine   Homatropine ψ-Tropine r-Ecgonine

reduction

Tropacocaine r-Cocaine.
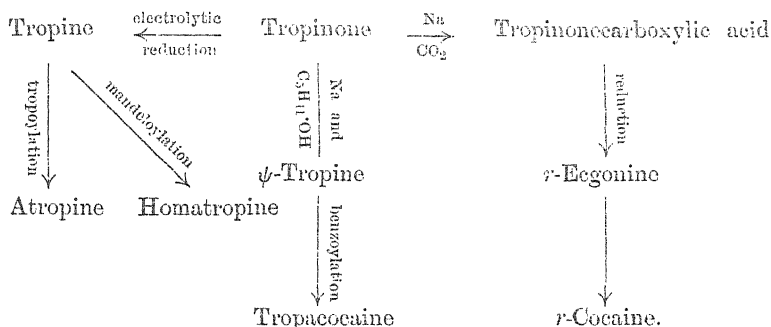
An examination of the details of the reactions involved in the above shows that it is improbable that cocaine would be synthesised from artificial tropinone, and that the feasibility of the preparation of atropine would depend on the elaboration of improved methods for the production of tropic acid. On the other hand, given readily accessible tropinone, the technical preparation of homatropine and tropacocaine would be a comparatively simple matter. By reason of the richness of the field of chemistry explored, the synthesis of tropine by Willstätter (*Annalen*, 1901, **317**, 204; 1903, **326**, 1) is classical, but the method employed, which it is unnecessary to recall in all its details, appears to be of too complicated a character to admit of development into an economical process. It is first of all necessary to obtain suberone, which is then converted through several stages into *cyclo*heptatriene, and finally into tropidine, ψ-tropine, tropinone, and tropine.

Nevertheless, an inspection of the formula of tropinone (I) discloses a degree of symmetry and an architecture which justify the hope that the base may ultimately be obtained in good yield as the product of some simple reaction and from accessible materials. By imaginary hydrolysis at the points indicated by the dotted lines, the substance may be resolved into succindialdehyde, methylamine, and acetone, and this observation suggested a line of attack of the problem which has resulted in a direct synthesis.

$$
\begin{array}{c}
\text{CH---CH}_2 \\
\text{CH}_2 \quad | \\
| \quad \text{NMe} \quad \text{CO} \\
\text{CH}_2 \quad | \\
\text{CH---CH}_2
\end{array}
\qquad
\begin{array}{c}
\text{CH----C:CH·C}_6\text{H}_3\text{:O}_2\text{:CH}_2 \\
\text{CH}_2 \quad | \\
| \quad \text{NMe} \quad \text{CO} \\
\text{CH}_2 \quad | \\
\text{CH----C:CH·C}_6\text{H}_3\text{:O}_2\text{:CH}_2
\end{array}
$$

(I.)   (II.)
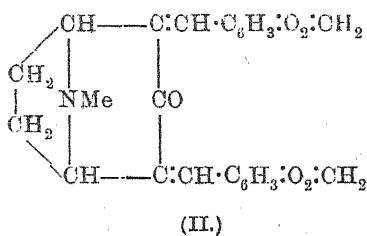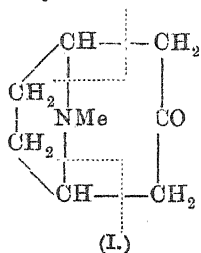
In searching for a method of synthesis of any substance, it is always convenient to be able to recognise the formation of traces of the desired product, and in the present instance none of the derivatives of tropinone already prepared was found to be so suitable for its detection as the dipiperonylidene derivative (II), which does not appear to have been hitherto described. With the aid of this highly characteristic compound it was proved that tropinone is obtained in small yield by the condensation of succindialdehyde with acetone and methylamine in aqueous solution. An improvement followed on the replacement of the acetone by a salt of acetonedicarboxylic acid. The initial product is a salt of tropinonedicarboxylic acid, and this loses two molecules of carbon dioxide with the formation of tropinone when the solution is acidified and heated.

$$
\begin{array}{c}
\text{CHO} \\
| \\
\text{CH}_2 \\
| \\
\text{CH}_2 \\
| \\
\text{CHO}
\end{array}
\; + \text{NH}_2\text{Me} \;\rightarrow\;
\begin{array}{c}
\text{CH·OH} \\
| \\
\text{CH}_2 \\
| \quad \text{NMe} \\
\text{CH}_2 \\
| \\
\text{CH·OH}
\end{array}
\; + \;
\begin{array}{c}
\text{CH}_2 \cdot \text{CO}_2\text{ca} \\
| \\
\text{CO} \\
| \\
\text{CH}_2 \cdot \text{CO}_2\text{ca}
\end{array}
\;\rightarrow
$$

$$
\begin{array}{c}
\text{CH}\text{---}\text{CH} \cdot \text{CO}_2\text{ca} \\
| \qquad | \\
\text{CH}_2 \qquad | \\
| \quad \text{NMe} \quad \text{CO} \\
\text{CH}_2 \qquad | \\
| \qquad | \\
\text{CH}\text{---}\text{CH} \cdot \text{CO}_2\text{ca}
\end{array}
\; + 2\text{HCl} \rightarrow
\begin{array}{c}
\text{CH}\text{---}\text{CH}_2 \\
| \qquad | \\
\text{CH}_2 \qquad | \\
| \quad \text{NMe} \quad \text{CO} \\
\text{CH}_2 \qquad | \\
| \qquad | \\
\text{CH}\text{---}\text{CH}_2
\end{array}
\quad
\begin{array}{l}
+ \text{CaCl}_2 \\[1em]
+ 2\text{CO}_2
\end{array}
$$
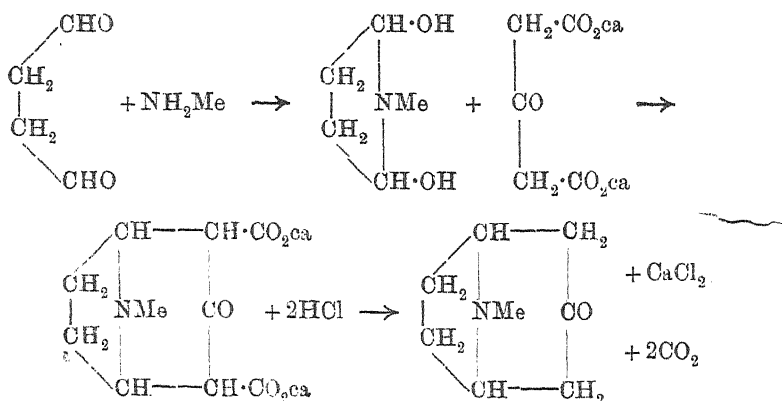
Tropinone was also obtained by the hydrolysis of the product of condensation of succindialdehyde with ethyl acetonedicarboxylate and methylamine in alcoholic solution. When more material is available it is hoped to institute a series of experiments with the object of defining the optimum conditions of the synthesis, and it will then be possible to state with more exactness the maximum yield obtainable. However, in spite of the small experience so far gained, an experiment is described in which the yield of dipiperonylidenetropinone from succindialdehyde was 42 per cent. of that theoretically possible. The method of synthesis of bicyclic bases which has been developed is probably of general application, and an attempt will be made to synthesise ψ-pelletierine by the condensation of glutardialdehyde with methylamine and a derivative of acetone.

EXPERIMENTAL.

Dipiperonylidenetropinone (Formula II).

Potassium hydroxide (5 grams) dissolved in water (20 c.c.) was added to tropinone (2 grams) and piperonal (6 grams) dissolved in alcohol (100 c.c.), and the solution was then boiled under reflux during fifteen minutes. The derivative crystallised during the course of the reaction, and, after the addition of water, was collected, washed with water and alcohol, and crystallised from ethyl acetate. The yield was quantitative:

0·1139 gave 0·2991 CO_2 and 0·0543 H_2O. C = 71·6; H = 5·3.
$C_{24}H_{21}O_5N$ requires C = 71·4; H = 5·2 per cent.

Dipiperonylidenetropinone separates from ethyl acetate in bright yellow needles melting at 214°, and is sparingly soluble in most organic solvents. If it is rubbed on the side of a test-tube and sulphuric acid added, the substance acquires a coppery lustre and then passes into an intense royal-blue solution. This becomes green and finally yellow on dilution with water. The salts of the substance are in general sparingly soluble, but the acetate dissolves readily in water to a bright orange-yellow solution. Yellow, crystalline precipitates of corresponding salts are obtained on the addition to such a solution of hydrochloric, hydrobromic, nitric, sulphuric, oxalic, or picric acid. The *hydrochloride* crystallises from hot water, in which it is sparingly soluble, in yellow, microscopic needles. The substance is decomposed by hydroxylamine in boiling alcoholic solution with the formation of piperonaloxime, and presumably of the oxime of tropinone.

The formation of the dipiperonylidene derivative serves as a means of detection of the merest traces of tropinone, and the test may be applied in the following manner. A solution which it is suspected contains the base may first be acidified and evaporated in a vacuum in order to remove possible volatile neutral impurities, such as acetone. Alcohol, an excess of piperonal, and potassium hydroxide are then added, and the solution heated on the steam-bath for two or three minutes and then poured into ether. The ethereal solution is washed with water and separated, and then agitated with a little dilute hydrochloric acid. If tropinone is present, the hydrochloride of the derivative is so obtained in a crystalline condition.

Synthesis of Tropinone from Succindialdehyde, Methylamine, and Acetone.

In this reaction, which has not yet been sufficiently investigated, it seemed that the tropinone could only be detected after the expiration of a brief period from the time of addition of the methylamine. If the reaction mixture was allowed to remain overnight, other basic ketones were obtained which condensed with piperonal and interfered with the recognition of the desired product. Succindialdoxime (7 grams) suspended in water (30 c.c.) was converted into succindialdehyde by means of nitrous fumes generated from nitric acid (D 1·3) and arsenious oxide according to the method developed by Harries (*Ber.*, 1901, **34**, 1494). Water (50 c.c.) was then added, and the nitrous and nitric acids neutralised by means of an excess of precipitated calcium carbonate. After the addition of acetone (5 grams), and then methylamine (4·5 grams) dissolved in water (20 c.c.), the mixture was allowed to remain during half an hour. The solution was acidified with hydrochloric acid and tested for tropinone by the method described above. The small quantity of the crystalline hydrochloride was collected, treated with a little aqueous ammonia, and the base crystallised from ethyl acetate. The yellow needles melted at 214°, and at the same temperature when mixed with a specimen of dipiperonylidenetropinone. The colour reactions of the two specimens in concentrated sulphuric acid were identical.

Synthesis of Tropinone from Succindialdehyde, Methylamine, and Ethyl Acetonedicarboxylate.

α-Succindialdehyde (1 gram) and ethyl acetonedicarboxylate (2·5 grams) were dissolved in alcohol (20 c.c.), and, after cooling in ice-water, a solution of methylamine (0·5 gram) in alcohol (10 c.c.) was gradually added during an hour. After remaining overnight at the ordinary temperature, the alcohol was removed by distillation in a vacuum, and the residue boiled with dilute sulphuric acid for half an hour and then evaporated in a high vacuum to small bulk. Potassium hydroxide was then added in excess, and the mixture distilled in a current of steam. The distillate was exactly neutralised with hydrochloric acid, concentrated, and the tropinone contained was identified as in the former example by conversion into the dipiperonylidene derivative, as described above. In this case also the identity of the synthetical product was established by the method of mixed melting points.

Synthesis of Tropinone from Succindialdehyde, Methylamine,
and Calcium Acetonedicarboxylate in Aqueous Solution.

Succindialdoxime (3·5 grams) was converted into dialdehyde in
the usual manner, and after the neutralisation with chalk the
solution was made up to 40 c.c. and mixed with acetonedicarb-
oxylic acid (4 grams) dissolved in water (20 c.c.) and neutralised
by the addition of calcium carbonate. Methylamine (from
8 grams of the hydrochloride) in water (10 c.c.) was then gradu-
ally added, and the whole allowed to remain at the ordinary
temperature during fifty hours. The liquid was filtered, acidified
with hydrochloric acid, and concentrated in a vacuum, using a
large flask on account of excessive frothing. The residue was
then rendered alkaline with sodium hydroxide and distilled in a
current of steam until the distillate was neutral to litmus. This
solution was then acidified with hydrochloric acid, concentrated
in a vacuum, and, after the addition of sodium hydroxide,
repeatedly extracted with ether. The combined ethereal extracts
were dried over potassium hydroxide, somewhat rapidly in order
to avoid the formation of salts, and the solvent removed by dis-
tillation. The residue gradually crystallised, oily impurities were
removed by contact with porous porcelain, and the substance was
recrystallised from light petroleum (b. p. 50—60°). Long,
flattened, pointed, colourless needles were obtained melting at 42°,
and at the same temperature when mixed with an equal quantity
of tropinone which had been obtained by the oxidation of tropine.

In every respect the two specimens were identical. For further
comparison the picrate was prepared. It crystallised from water
in canary-yellow needles melting and decomposing at 218—220°
alone or when mixed with tropinone picrate, which had in this
case been obtained by the oxidation of ecgonine.

The oil separated from the crystalline base was recovered from
the plate by extraction with ether, and after removal of the
solvent, piperonal, alcohol, and potassium hydroxide were added
and the mixture heated during five minutes on the steam-bath.
The precipitate obtained on the addition of water was collected,
washed with alcohol, and then crystallised from ethyl acetate.
Dipiperonylidenetropinone melting at 214° was thus isolated.

In the above experiment there is some uncertainty as to the
amount of succindialdehyde started from, since the author, no
doubt through lack of practice, has never been able to obtain the
high yield claimed by Harries of from 70 to 80 per cent. In
order, therefore, to gain some idea of the yield of tropinone from
succindialdehyde, the following experiment was made, but the

H H*

conditions of the synthesis are still under investigation, and it is hoped that even better results may ultimately be obtained.

A solution of succindialdehyde containing inorganic salts was first prepared in the usual way and then distilled in a current of steam. The distillate was concentrated in a high vacuum until, as it later appeared, about a 10 per cent. aqueous solution was obtained. Ten c.c. of this solution were diluted with water, and the dialdehyde was converted into the diphenylhydrazone, as described by Harries (*Ber.*, 1902, **35**, 1188). The solution contained 0·96 gram of succinaldehyde. Twenty-five c.c. (containing 2·42 grams of the dialdehyde) were mixed with a solution of acetonedicarboxylic acid (6 grams) in water (75 c.c.) to which a sufficient excess of precipitated calcium carbonate had been added, and after cooling in ice-water, methylamine (3 grams) in water (10 c.c.) was gradually introduced. The reaction was allowed three days for completion, and the liquid was then acidified to Congo paper with hydrochloric acid and concentrated in a high vacuum. The residue was dissolved in alcohol and the tropinone converted into dipiperonylidene derivative in the usual manner. The product was collected, well washed with water and a little alcohol, and dried at 100°. It weighed 4·1 grams and was free from inorganic impurities. The substance was identified as dipiperonylidenetropinone, and the above data show that the yield of tropinone from succindialdehyde in this experiment was 42 per cent. of that theoretically possible.

The possibility that tropinone might result from the condensation of succindialdehyde or a derivative with acetone or a derivative and methylamine or by the addition of methylamine to a *cyclo*heptadienone occurred simultaneously to Professor A. Lapworth and the author, and a joint research was contemplated, but Dr. Lapworth's preoccupation with more urgent investigations did not allow him to undertake this fresh experimental work.

LXIV.—*The Pungent Principles of Ginger. Part I. A New Ketone, Zingerone (4-Hydroxy-3-methoxyphenylethyl Methyl Ketone) occurring in Ginger.*

By Hiroshi Nomura.

THRESH assigned the name " gingerol " to the pungent principle of ginger, and Garnett and Grier (*Pharm. J.*, 1907, [iv], **25**, 118) claimed to have isolated it. However, no account of an investigation of its composition and constitution is to be found in the literature, and the present work was undertaken to determine the constitution of the pungent principle.

The new ketone, to which the name " zingerone " is assigned, was obtained by extracting ginger with ether, followed by the treatment described on p. 770, and was proved to have the formula $C_{11}H_{14}O_3$. It yields monobenzoyl and monoacetyl derivatives, and the existence of one methoxyl group in it was proved. The methyl derivative, $C_{12}H_{16}O_3$, is readily converted into its oxime, $C_{12}H_{17}O_3N$, by hydroxylamine, which points to the presence of one carbonyl group. When the methyl derivative is oxidised with potassium permanganate in alkaline solution, veratric acid is obtained, and therefore the new ketone must be a $1:3:4$-derivative of benzene.

Since sodium hydrogen sulphite combines with the new ketone and with its methyl derivative and the latter is oxidisable with difficulty by an ammoniacal solution of silver nitrate, the group, $CO \cdot CH_3$, appears to exist in both compounds. If this is the case, the constitutional formula of the methyl derivative must be either (I) or (II), and the constitution of the original ketone must be

COMe·CH₂·CH₂⟨OMe⟩OMe   COMe·CHMe⟨OMe⟩OMe

(I.)   (II.)
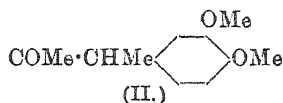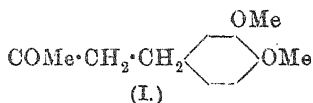
(III), (IV), (V), or (VI), according as the methyl derivative has the constitution (I) or (II) respectively. In order to decide between

COMe·CH₂·CH₂⟨OMe⟩OH   COMe·CH₂·CH₂⟨OH⟩OMe

(III.)   (IV.)

COMe·CHMe⟨OMe⟩OH   COMe·CHMe⟨OH⟩OMe

(V.)   (VI.)
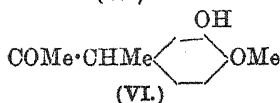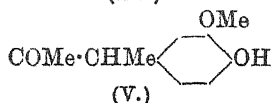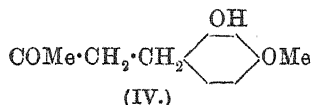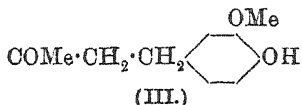
these, the following two methods may be used.

I. The constitution of the methyl derivative may be determined by examining its products of oxidation by sodium hypobromite or hypochlorite. If the constitutional formula of the methyl derivative is once determined, that of the original ketone could be determined by the introduction of the ethyl group and subsequent oxidation.

II. If the constitution of the methyl derivative is (I), it could be synthesised by the reduction of the condensation product of vanillin and acetone, and subsequent methylation according to the following scheme:

$$C_6H_3(OH)(OMe) \cdot CHO \xrightarrow{acetone} C_6H_3(OH)(OMe) \cdot CH \colon CH \cdot COMe \xrightarrow{H_2}$$

$$C_6H_3(OH)(OMe) \cdot CH_2 \cdot CH_2 \cdot COMe \xrightarrow{methylation}$$
$$C_6H_3(OMe)_2 \cdot CH_2 \cdot CH_2 \cdot COMe.$$
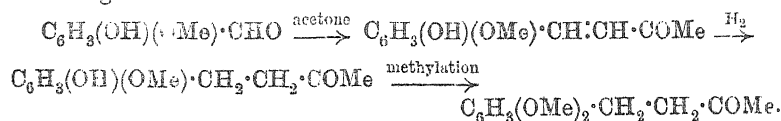
According as the intermediate product in this synthesis agrees with the new ketone or not, the constitution of the latter must be either (III) or one of (IV), (V), and (VI). In the latter case, if the methyl derivative is identical with the above synthetical 3:4-dimethoxyphenylethyl methyl ketone, the constitution of the new ketone should be (IV). If this experiment fails to yield the methyl derivative, the constitutional formula of the latter is necessarily (II), and that of the new ketone can be determined by the oxidation of its ethyl derivative.

Since the yield of the ketone from ginger is poor, the second method is preferable to the first. Fortunately, by the reduction of the condensation product of vanillin and acetone, a substance identical with the new ketone was obtained. Its identity was further proved by comparing its benzoyl derivative and the oxime of its methyl ether with the corresponding derivatives of the naturally occurring ketone.

The constitution of the new ketone was, moreover, confirmed by the first method, namely, by the production, from the methyl derivative, of bromoform and β-3:4-dimethoxyphenylpropionic acid by oxidation with sodium hypobromite, and by the formation, from the ethyl derivative, of ethylvanillic acid by means of potassium permanganate in alkaline solution. There is no doubt, therefore, that the constitution of the new ketone is (III). The investigation of the other pungent principle and the synthesis of the substances analogous to the new ketone are now in progress.

EXPERIMENTAL.

Dry powdered ginger (367 kilos.) was extracted with ether in the cold and the ethereal extract evaporated to a syrupy consistency. The syrup was dissolved in a small quantity of ether and

shaken with 2 per cent. sodium hydroxide for three hours. The quantity of sodium hydroxide solution required for the extraction of the pungent principles from the syrup was determined by a preliminary experiment, 500 c.c. of 2 per cent. sodium hydroxide being necessary for 100 grams of the syrup. The pungent principles in the alkaline solution were deposited by means of carbon dioxide free from hydrochloric acid and extracted with ether. The ethereal solution was washed with $2N$-sodium carbonate solution to remove any acid, and then with water until the alkaline reaction disappeared, dried over anhydrous sodium sulphate, and evaporated. The yield of residual oil was about 1 per cent. of the original ginger. It was distilled under 0·5—1 mm. pressure until the temperature of the oil-bath reached 320°, after the previous distillation of volatile substance under 13—23 mm. pressure. The whole of the distillate was diluted with ether and shaken with an excess of a concentrated solution of sodium hydrogen sulphite, whereby the bisulphite compound of the new ketone separated. This was collected, washed with ether until the washing was colourless, and decomposed with a concentrated solution of sodium carbonate. The oil was extracted with ether, the ethereal solution washed several times with water, dried over anhydrous sodium sulphate, and evaporated. The yield of oil thus obtained was 0·04 per cent. of the original material. On cooling and continuous agitation with a minute quantity of the solid ketone, the oil solidified to a somewhat brown mass, which melted at 40—41° after recrystallisation from light petroleum (b. p. 50—70°) or a mixture of ether and light petroleum. The colourless crystals thus purified gave the following results on analysis :

0·0944 gave 0·2350 CO_2 and 0·0629 H_2O.   C $= 67·89$; H $= 7·45$.

0·0900 „   0·2243 CO_2 „ 0·0600 H_2O.   C $= 67·97$; H $= 7·46$.

0·2559 „   0·2812 AgI.   Me $= 7·03$.

0·1615 in 19·64 benzene gave $\Delta t = -0·217°$.   M.W. $= 189$.

$C_{11}H_{14}O_3$ requires C $= 68·00$; H $= 7·27$; IMe $= 7·74$ per cent.

M.W. $= 194$.

Zingerone gives a red coloration with Millon's reagent, dissolves to a green-coloured solution with alcoholic ferric chloride, and reduces ammoniacal silver nitrate solution on warming. There is no visible decomposition on shaking the ketone with 2 per cent. sodium hydroxide for several hours.

The phenylhydrazone and semicarbazone were not obtained in the pure state, owing to the instability of the compounds and the small quantities of ketone used for the preparation.

Benzoyl Derivative.—Half a gram of zingerone dissolved in 30 c.c. of 5 per cent. sodium hydroxide solution was shaken with

3 c.c. of benzoyl chloride for two hours; the precipitate was collected and washed with water. After being dried in the desiccator, the substance was twice recrystallised from absolute alcohol with the addition of animal charcoal, when it separated in colourless crystals melting at 126—127°. The yield was 0·35 gram after one crystallisation:

0·1058 gave 0·2803 CO_2 and 0·0590 H_2O. $C = 72·25$; $H = 6·24$.

$C_{18}H_{18}O_4$ requires $C = 72·45$; $H = 6·08$ per cent.

Acetyl Derivative.—Seven grams of zingerone were boiled for one hour under a reflux condenser with 7 grams of fused sodium acetate and 25 grams of acetic anhydride. After the removal of the excess of acetic anhydride under diminished pressure, the product was extracted with ether and the ethereal solution washed with a dilute solution of sodium carbonate and then with water until it became free from alkali. The dried ethereal solution was evaporated and the residual oil purified by distillation under diminished pressure. During the first distillation, almost the whole quantity distilled at 202—206°/14 mm., the main portion distilling at 204—206°. The yield was 7·1 grams. On repeating the operation, the substance boiled constantly at 204—205° under the same pressure:

0·1787 gave 0·4317 CO_2 and 0·1107 H_2O. $C = 65·89$; $H = 6·93$.

$C_{13}H_{16}O_4$ requires $C = 66·07$; $H = 6·83$ per cent.

On allowing it to remain for a few days, the oil solidified and melted at 40—42°, the melting point of the original ketone. It differs, however, from the latter in that the crystals give no coloration with ferric chloride in alcoholic solution and liquefy when mixed with the ketone. It is sparingly soluble in light petroleum, but readily so in alcohol or benzene. The result of the oxidation of this acetyl derivative with potassium permanganate in the presence of magnesium sulphate was unsatisfactory.

Methylzingerone.[*]—The ketone (5·7 grams) was dissolved in 30 c.c. of 5 per cent. sodium hydroxide solution and shaken with 3·5 c.c. of methyl sulphate for half an hour. After removing the unchanged ketone by shaking with 5 c.c. of 10 per cent. sodium hydroxide solution, the product was extracted with ether, the ethereal solution washed several times with water, and shaken with a concentrated solution of sodium hydrogen sulphite. The

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[*] When the determination of the constitution of the ketone was complete and that of the other pungent principle in progress, the compounds which correspond with the methyl derivative and its oxime were synthesised by Kaufmann and Radosević (*Ber.*, 1916, **49**, 675). The description of the melting points of these compounds is in agreement with those of the above methyl derivative and its oxime respectively.

bisulphite compound was collected, washed with ether, decomposed with sodium carbonate, and the product extracted with ether. The ethereal solution was washed with water, dried over anhydrous sodium sulphate, and evaporated. The residual oil was then distilled under diminished pressure, when almost the whole quantity passed over at 188—189°/17·5 mm. The yield was 2·8 grams. On repeating the distillation, a colourless oil boiling at 186°/16 mm. was obtained:

0·1258 gave 0·3166 CO_2 and 0·0885 H_2O.   C = 68·64 ; H = 7·87.
$C_{12}H_{16}O_3$ requires C = 69·19 ; H = 7·75 per cent.

After several months, the oil partly solidified. On stirring with a glass rod, the whole solidified with the evolution of heat, and melted at 55—56°. The compound was oxidised with difficulty by an ammoniacal solution of silver nitrate.

Methylzingeroneoxime.—A mixture of methylzingerone (1 gram), hydroxylamine hydrochloride (0·35 gram), and sodium acetate (0·7 gram) was dissolved in dilute alcohol and boiled for two hours under a reflux condenser. In order to isolate the product, the alcohol was removed by gentle evaporation, the oily oxime, which, however, readily solidified, collected, washed with water, and dried. The yield was 1 gram. The crystals were several times recrystallised from dilute methyl alcohol with the addition of animal charcoal, when they separated in colourless needles melting at 93—93·5°:

0·1395 gave 8·04 c.c. N_2 at 22° and 754·5 mm.   N = 6·45.
$C_{12}H_{17}O_3N$ requires N = 6·28 per cent.

Ethylzingerone.—Seven grams of zingerone and 2·1 grams of potassium hydroxide were dissolved in warm methyl alcohol, and the residue left on the evaporation of the methyl alcohol was heated for three hours under a reflux condenser with 30 c.c. of absolute alcohol and 20 grams of ethyl iodide. The alcohol and the excess of ethyl iodide were removed, when a brown mass separated, which was washed with 2 per cent. sodium hydroxide to remove the unchanged ketone, and then with water until it became neutral. The mass was now crystallised from dilute alcohol and then from light petroleum (b. p. below 60°) with the addition of animal charcoal. The yield was 6 grams after one crystallisation from dilute alcohol. The crystals thus purified were colourless and gave the following results on analysis:

0·1523 gave 0·3926 CO_2 and 0·1160 H_2O.   C = 70·30 ; H = 8·52.
$C_{13}H_{18}O_3$ requires C = 70·23 ; H = 8·16 per cent.

The compound melts at 66°, and is soluble in ether or methyl or ethyl alcohol, but insoluble in water.

Oxidation of Methylzingerone with Potassium Permanganate.

The compound (2·3 grams; 1 mol.) and 100 c.c. of 2N-sodium carbonate solution were heated under a reflux condenser, and 390 c.c. of a 3 per cent. solution of potassium permanganate (corresponding with 5 mols. of oxygen) were slowly run in. The boiling was continued until the colour of the permanganate disappeared, and the product was cooled and filtered from the precipitated manganese dioxide. The filtrate and washings of the manganese dioxide were treated with ether to remove any unchanged methylzingerone, evaporated to a small bulk, and acidified with hydrochloric acid, when a yellow acid (1·8 grams) separated, which after recrystallisation from water with the addition of animal charcoal and drying at 100—110° melted at 180—181°. The acid prepared by the above method was colourless (Found, C=59·13; H=5·82. $C_9H_{10}O_4$ requires C=59·31; H=5·53 per cent.), and the melting point was not changed by admixture with veratric acid.

Oxidation of Ethylzingerone with Sodium Hypochlorite.

This oxidation was carried out in an exactly similar manner to that employed in the oxidation of the methyl derivative. The acid obtained melted at 195—196° (Found, C=61·39; H=6·31. $C_{10}H_{12}O_4$ requires C=61·20; H=6·17 per cent.) and did not depress the melting point of ethylvanillic acid.

Oxidation of Methylzingerone with Sodium Hypochlorite.

Two grams of the substance were suspended in an excess of an alkaline solution of sodium hypochlorite and warmed on the water-bath until a clear solution was obtained and no chloroform evolved. The solution was rapidly cooled, acidified with sulphurous acid, evaporated to a small bulk, and extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate, evaporated, and the residue was recrystallised from water, from which two different acids were obtained.

The one melted at 180—181° after drying at 100—110°, and this melting point was not depressed by admixture with veratric acid. The other melted at 95—99°, but it could not be purified owing to lack of substance. It is, however, probable that the substance is β-3 : 4-dimethoxyphenylpropionic acid (m. p. 98—99°).

Oxidation of Methylzingerone with Sodium Hypobromite.

The compound (3·1 grams) was shaken for two hours with an alkaline solution of sodium hypobromite, which was prepared by dis-

solving 2·3 c.c. of bromine in ice-cooled sodium hydroxide solution (6 grams in 100 c.c. of water), when the reaction of the hypobromite vanished. The product was then extracted with ether, and the ethereal solution (A) and the alkaline solution (B) were treated in the following way.

(A) The ethereal solution was washed with water until it became free from alkali, and the greater part of the ether evaporated. The residual solution was freed from any unchanged methylzingerone by shaking with a concentrated solution of sodium hydrogen sulphite, washed with sodium carbonate solution, and then with water until free from alkali. The ethereal solution thus purified was dried over anhydrous sodium sulphate and evaporated. The residual oil (2·1 grams) on distillation gave 0·8 gram of oil boiling at 147—148° and possessing the characteristic odour of bromoform.

(B.) After evaporating to a small bulk, the aqueous solution was acidified with hydrochloric acid, extracted with ether, washed several times with a saturated solution of sodium chloride, and dried over anhydrous sodium sulphate. On distilling off the ether from the ethereal solution, 2·6 grams of a yellow syrup were obtained, which did not solidify on keeping for a few days. The syrup was now dissolved in a small quantity of $2N$-sodium carbonate solution, the solution digested with animal charcoal, filtered, and acidified with hydrochloric acid, when a yellow oil separated which on keeping overnight partly solidified to crystals. The crystals were collected, freed from the last traces of oil by draining on a porous tile, and recrystallised from water with the addition of animal charcoal. The crystals thus purified melted at 98—99° after being dried over sulphuric acid in the desiccator, and were proved to have the constitution of β-3:4-dimethoxyphenylpropionic acid by the mixed melting-point method. The yield of the impure crystals was 0·55 gram.

Synthesis of Zingerone (4-Hydroxy-3-methoxyphenylethyl Methyl Ketone), $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_6H_3(OMe) \cdot OH$.

The intermediate compound in this synthesis, namely, 4-hydroxy-3-methoxystyryl methyl ketone, $CH_3 \cdot CO \cdot CH:CH \cdot C_6H_3(OMe) \cdot OH$, has been described by Francesconi and Cusmano (*Gazzetta*, 1908, **38**, ii, 70), who, however, give no details of its preparation. It was therefore synthesised in the following way.

Seventy c.c. of 10 per cent. sodium hydroxide solution were added to a solution of 25 grams of vanillin in 100 c.c. of acetone, and after being allowed to remain for four days, the solution was acidified with dilute hydrochloric acid, when a yellow precipitate was obtained. The precipitate was collected, washed with water

until free from chloride, and crystallised from dilute alcohol, from which it separated in yellow crystals melting at 128—129°. The yield was 28 grams after one crystallisation.

Six grams of this compound were suspended in 100 c.c. of absolute ether and reduced for nine hours by means of hydrogen in the presence of platinum black. The hydrogen absorbed was about 800 c.c. (at 23—24° and 752—754 mm.). After filtering off the platinum black, the filtrate and ethereal washings were evaporated, and the residual oil on distillation boiled constantly at 187—188°/14 mm. The yield was 4·8 grams. The oil was twice recrystallised from a mixture of ether and light petroleum (b. p. below 60°). The crystals thus obtained melted at 40—41°:

0·1629 gave 0·4058 CO_2 and 0·1090 H_2O. $C = 67·94$; $H = 7·49$.

0·1244   ,,   0·3113 CO_2 ,,   0·0850 H_2O. $C = 68·25$; $H = 7·64$.

$C_{11}H_{14}O_3$ requires $C = 68·00$; $H = 7·27$ per cent.

The substance sustained no lowering of the melting point by mixing with the naturally occurring ketone. The benzoyl derivative and the oxime of the methyl ether melted respectively at 126—127° and 93—93·5°, and these melting points were not altered when the respective compounds were mixed with the corresponding derivative of the naturally occurring ketone.

The isolation of zingerone was made for the first time in the laboratory of the Agricultural College, Tokyo Imperial University, under Professor Umetaro Suzuki, and after my coming to the Science College, Tohoku Imperial University, the work was resumed under the guidance of Professor Riko Majima. Since then, the separation of the ketone has been effected more easily and its constitution studied with satisfactory results. The author wishes to express his hearty thanks to the professors for their kind suggestions.

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LXV.—*The Pungent Principle of Ginger. Part I. The Chemical Characters and Decomposition Products of Thresh's "Gingerol."*

By Arthur Lapworth, (Mrs.) Leonore Kletz Pearson, and Frank Albert Royle.

The pungent principles of ginger, the rhizome of *Zingiber officinale*, were studied by Thresh ("Year-Book of Pharmacy," 1879, 426; 1884, 516; *Pharm. J.*, 1882, [iii], 12, 721). The pungency was attributed to an active principle, "gingerol," an inodorous substance having the general characters of the class of compounds now known as "oleo-resins," which he isolated by means of a somewhat complicated fractionation of the alcoholic extract of the drug. He attributed to it the approximate formula xC_5H_8O, and found that on oxidation with chromic acid it yielded "apparently" acetic and caproic acids ("Year-Book of Pharmacy," 1884, 520), together with a volatile oil. Thresh seems to have abandoned the work at an early stage.

Garnett and Grier (*Pharm. J.*, 1907, [iv], 25, 118; "Year Book of Pharmacy," 1909, 344; compare also *ibid.*, 1907, 443) re-examined the pungent oleo-resin, gingerol, and simplified and improved the method of isolation and purification used by Thresh. They fractionated the crude mixture of oleo-resins with the aid of petroleum, and ultimately obtained a "clear, viscous oil, of a pale straw colour, distilling within a range of 235° C. to 250° C.," the pressure referred to being 18 mm. They add: "It could not be assumed, without further proof, that this body" (that is, the distillate) "was not either a product of destructive distillation, or that it was not contaminated with such products"; they showed, however, that the distillate had the pungency and many other characteristics of the original gingerol. In the course of their experiments they noted that gingerol was possessed of phenolic characters, gave a green colour in alcoholic solution with ferric chloride, a precipitate with bromine, and that the solution in alkalis, especially when warm, undergoes a change which results in a loss of the pungent character in the dissolved oil. The latter observation was made use of in devising a simple means of distinguishing between extracts of ginger and of capsicum respectively, as the latter is not affected in pungency by alkalis and is often used to adulterate or fraudulently to replace the former.

The present authors were invited by Messrs. Garnett and Grier to continue the work on gingerol, and carried out the experiments described in this paper with a large sample of an alcoholic extract

ginger, the most pungent variety on the market. This
kindly made for them by James Woolley and Sons,

Method Used in Isolating Gingerol.

The residue from the alcoholic extract was treated repeatedly
with aqueous alcohol of 35 per cent. strength, which is considerably
weaker than was used by Thresh or by Garnett and Grier; it was
found that this dissolved the inactive resins much less freely and
gave a more rapid separation. Alcohol was removed from the clear
extract by evaporation in a vacuum at the lowest possible tempera-
ture, the oil which separated being freed from as much water as
possible and re-extracted with alcohol of about 50 per cent.
strength. Milk of lime was then added, as suggested by Thresh,
until only a very slight deposition of calcium compounds took place,
when the whole was allowed to settle, and the clear liquid made
neutral to litmus by addition of dilute hydrochloric acid, and again
freed from alcohol by distillation under diminished pressure. The
resulting oil was separated from the bulk of water by decantation,
dissolved in a solvent, such as chloroform, which was subsequently
dried, and removed by evaporation. The dry crude gingerol was
then extracted fractionally with hot petroleum, and those portions
retained which dissolved freely in the hot petroleum, but were
re-deposited on cooling. After removing all traces of petroleum,
the "refined gingerol" was obtained as a viscous, faintly yellow
oil, entirely soluble in dilute aqueous alkali, and generally having
all the properties assigned to the material by Garnett and Grier.

Many various methods were tried for the further purification
of the refined gingerol, but even the best samples obtained were
almost certainly not homogeneous materials, and could be frac-
tionated by means of light petroleum into portions having some-
what different solubilities. As many of the less soluble fractions
of the oils shared the characters of the most soluble portion, it
was suspected that gingerol either tends to polymerise or to
decompose into simpler products, such as those mentioned later,
with subsequent recombination of these to products more complex
than gingerol proper.

The most highly purified samples obtained were distilled in a
cathode-ray vacuum; they passed over almost completely when the
temperature of the bath was 135—140°, and the distillate was in
such cases a clear, faintly yellow oil. Even under these conditions
there was evidence of slight decomposition (odour of fatty alde-
hydes) and only traces of camphoraceous solid separated from the
oil after many months.

Messrs. Garnett and Grier directed the authors' attention, at the commencement of the work, to the fact that some samples of gingerol give a crystalline product when they are shaken with a solution of sodium hydrogen sulphite; the present authors found that the most highly purified samples do not give any such product, but do so after they have been distilled or otherwise somewhat strongly heated, or treated with dilute alkalis under certain conditions.

Analysis of the best samples of gingerol obtained gave:

$C = 71\cdot4$; $H = 9\cdot2$; $C = 71\cdot6$; $H = 9\cdot4$.

$\qquad$ $C_{17}H_{26}O_4$ requires $C = 69\cdot4$; $H = 8\cdot8$ per cent.

$\qquad$ $C_{18}H_{28}O_4$ $\quad$,, $\quad$ $C = 70\cdot1$; $H = 9\cdot1$,, $\quad$,,

Thresh found: $C = 71\cdot27$, $71\cdot39$, $71\cdot43$, and $H = 9\cdot61$, $9\cdot82$, $9\cdot52$.

Determination of methoxyl in gingerol:

Found: $Me = 7\cdot3$, $7\cdot7$. $1MeO$ in $C_{17}H_{26}O_4$ requires $MeO = 10\cdot5$; in $C_{18}H_{28}O_4$ $MeO = 10\cdot05$ per cent. (This, for reasons which appear later, would indicate a purity of only about 75 per cent.)

Other Properties of " Gingerol."

The presence of one hydroxyl group at least is indicated by the phenolic character of gingerol. The alkaline solution when treated with benzoyl chloride, benzenesulphonyl chloride, and similar compounds or with chloroformic esters, deposited neutral, non-pungent oils, which did not show any signs of assuming crystalline form. The oil yielded no crystalline oxime or semicarbazone, although there was some evidence that a nitrogenous compound was formed on treating it with hydroxylamine. Slight heat was evolved on mixing phenylhydrazine with gingerol; but neither with that substance nor with substituted phenylhydrazines, benzyl- or naphthylhydrazines did gingerol give any crystalline derivatives.

The sole derivative of gingerol which was obtained in definitely crystalline form was its monomethyl derivative. As this was easily purified, whilst the purity of gingerol could not be guaranteed, all conclusions as to the true composition and constitution of " gingerol " have been based on an examination of " methylgingerol."

Preparation and Properties of " Methylgingerol."

Refined gingerol is dissolved in methyl alcohol and treated with methyl sulphate and potassium hydroxide successively. From the product, ether extracts a neutral oil which deposits crystals, and these can be drained and recrystallised from light petroleum. ~~~out 15 grams of methylgingerol melting at 64° can be obtained onta~~ n 24 grams of the best gingerol which the authors have pre-

pared; this is again indicative of the mixed characters of gingerol.

Analyses of different samples of methylgingerol gave the following results:

$C = 70.21$, 70.44, 70.17, 70.15, 70.05, 70.2.

$H = 8.64$, 9.08, 8.92, 9.46, 9.19, 9.0.

$MeO = 22.6$, 19.8, 19.8.

Qualitative tests and analysis by the Dumas method showed that no nitrogen was present:

$C_{18}H_{28}O_4$ requires $C = 70.1$; $H = 9.2$; $2MeO = 20.1$ per cent.

$C_{19}H_{28}O_4$,, $C = 71.2$; $H = 8.75$; $2MeO = 20.0$,, ,,

$C_{19}H_{30}O_4$,, $C = 70.75$; $H = 9.4$; $2MeO = 19.9$,, ,,

The molecular weight of "methylgingerol" was determined by the cryoscopic method in benzene. The numbers obtained were 271, 309, 308, 316, 323, 323, the numbers required for $C_{18}H_{28}O_4$ and $C_{19}H_{30}O_4$ being 308 and 322 respectively.

"Methylgingerol" crystallises in slender needles melting at 64°. It is insoluble in cold alkalis or acids, but is altered by these if hot (compare later). It is also slowly decomposed when it is heated above 150°, and rapidly near its boiling point—the odour of fatty aldehydes becoming perceptible.

It is optically active in 2 per cent. solution in chloroform, having $[\alpha]_D^{21} + 27.3°$.

Ketonic Properties of "Methylgingerol."

Methylgingerol appears to be attacked slowly by phenylhydrazine, etc., but the products were not obtained in a crystalline form. When it is warmed in alcoholic solution with hydroxylamine hydrochloride and sodium acetate, however, it gives a crystalline derivative which was obtained in slender needles from light petroleum.

Found: $C = 64.9$, 64.0, 64.1, 64.5; $H = 9.1$, 9.4, 9.0, 9.2; $N = 4.3$.

$C_{18}H_{29}O_4N,H_2O$ requires $C = 63.3$; $H = 9.1$; $N = 4.1$ per cent.

$C_{19}H_{31}O_4N,H_2O$,, $C = 64.2$; $H = 9.3$; $N = 3.9$,, ,,

The analyses indicate that the substance is *methylgingerol oxime hydrate*. When heated at 110—115° for four hours it lost 4.09 per cent. in weight, whilst the theoretical loss for $1H_2O$ is about 5.1. The treatment was not pressed, as there were signs of more profound decomposition.

The oxime dissolves in cold hydrochloric acid and is reprecipitated by alkali. When it is hydrolysed by acids it is reconverted into methylgingerol and hydroxylamine, the former, after recrystallisation, being unchanged in melting point. When this oxime subjected to Piloty's test for ketoximes, it gives a definite posit

reaction, a yellowish-green coloration being obtained in the ethereal layer. The whole of the phenomena observed during the various stages of the test are not to be distinguished from those observed when the related methylzingeroneoxime (p. 786) is treated in the same way.

Methylgingerol is at once attacked by chromic acid, giving a black compound (chromate?), much as many alcohols (for example, menthol) do. It is instantly attacked by phosphorus pentachloride or thionyl chloride and hydrogen chloride is evolved. A cold solution of methylgingerol in chloroform does not at once discharge the colour of bromine in the same solvent, but an action takes place only on heating, when hydrogen bromide is evolved. Pure methylgingerol is also stable towards cold permanganate in acetone solution; even after long heating with excess of this reagent, the bulk of the compound is recovered unchanged, and this fact may be utilised to purify the crude substance from more easily oxidisable materials. Prolonged action of hot aqueous permanganate destroys methylgingerol, fatty acids, veratric acid, and carbon dioxide being formed. It is not reduced in the cold by sodium amalgam or by hydrogen in the presence of colloidal platinum or palladium.

Tests for the Hydroxyl Group in Methylgingerol.

In order to ascertain whether methylgingerol contained free hydroxyl, the compound, in amyl ether, was treated with magnesium methyl iodide in the same solvent in an apparatus similar to that used by Sudborough for the determination of hydroxyl by this method. On mixing the two solutions, a white precipitate of an additive compound was instantly formed, but no trace of methane or other permanent gas was detected, even when excess of magnesium methyl iodide was used and the temperature was raised nearly to 100°. The experiment was repeated several times and always gave the same result. On the other hand, methylgingerol is quickly attacked by cold acetyl chloride, thionyl chloride, or phosphorus chlorides, and hydrogen chloride is evolved; this change takes place rapidly on heating. Again, when methylgingerol is sealed up in a tube with rather less than one molecular proportion of phenylcarbamide, it does not at first dissolve in it, but after some weeks in the cold the solid disappears and a clear, viscid liquid is formed in which the odour of phenylcarbamide cannot be detected. No crystalline derivatives were isolated in either instance, but the observations, more especially the last one, are very difficult to explain, except on the assumption that methylgingerol contains a free hydroxyl group, and the same remark applies to its

behaviour with chromic acid. The failure of the substance to give methane with magnesium methyl iodide is possibly due to the insolubility of the additive product which the reagent seems to form by uniting with the compound at the ketonic carbonyl group.

Oxidation of Gingerol with Chromic Acid. Formation of n-Heptoic and (probably) n-Hexoic Acid.

Thresh oxidised gingerol with chromic acid and obtained what he considered to be, probably, acetic and caproic (hexoic) acids, together with a volatile oil (loc. cit., 1884, 520). The present authors dissolved about 50 grams of refined gingerol in warm acetic acid of about 90 per cent. strength, and added solid chromic acid in small quantities at a time until further addition caused no immediate effervescence. The liquid was then subjected to distillation in a current of steam, the latter portions of the distillate being collected, extracted with ether, and the latter evaporated. The residue was rendered alkaline with sodium hydroxide and once more treated with a current of steam, when a small quantity of a neutral oil, probably identical with that mentioned by Thresh, passed over. This oil was not examined more closely, but the alkaline residues in the flask were acidified, extracted with ether, and the latter dried and fractionated. After some water and acetic acid had distilled, the main bulk of the residue, amounting to about 7 grams, passed over at 210—225° and was clearly a mixture of saturated fatty acids; on refractionation, the range was not appreciably altered (n-hexoic acid boils at 205°; n-heptoic acid at 223°). The fractions, except the highest and lowest, were mixed, and a sample was titrated with standard alkali in the presence of phenolphthalein as indicator. The equivalent found was 125, which corresponds with about one part of hexoic acid and two parts of heptoic acid. The portion of the oxidation product which was not volatile in steam was small and nothing definite could be isolated from it.

Oxidation of Methylgingerol. Formation of Fatty Acids and Veratric Acid.

As the presence of phenolic hydroxyl in gingerol evidently led to destruction of the aromatic portion of the molecule by the oxidising agent, the oxidation of 8 grams of methylgingerol by means of chromic acid in acetic acid solution was carried out and the products were worked up as in the immediately preceding description. A mixture of fatty acids was obtained as before, but from that part of the product which was not volatile in steam about 0·9 gram of acid was obtained on extraction with ether. This, when

purified by crystallisation from hot water, formed flat needles melting at 180—181°, and its equivalent, found by titration with standard alkali, using phenolphthalein as indicator, was 184. It was readily identified as veratric acid (equivalent = 182).

Fusion of Gingerol with Potassium Hydroxide. Formation of Protocatechuic Acid.

Stenhouse and Groves (T., 1877, **31**, i, 533) found protocatechuic acid in the product obtained by fusing crude ginger resins with potassium hydroxide. The present authors tried the same experiment with refined gingerol, and although the great bulk of the material carbonised, a small quantity of protocatechuic acid was isolated from the product and identified.

Action of Heat and of Hydrolytic Agents on Gingerol. Formation of Aliphatic Aldehydes (mainly n-Heptaldehyde) and a Ketone, "Zingerone."

It has been mentioned that Messrs. Garnett and Grier had noticed that some specimens of gingerol gave a quantity of mixed crystalline solids when shaken with aqueous sodium hydrogen sulphite. The present authors find that this is only the case with old specimens or material which have been heated alone or with acids or alkalis, and such specimens have a peculiar odour whilst pure ones are practically odourless.

If a sample of gingerol which has been distilled under diminished pressure is subjected to a current of steam, a certain quantity of a volatile oil, with an odour resembling œnanthol (heptaldehyde), passes over. This, if extracted from the distillate by ether, is obtained as a colourless oil. If the ethereal solution is shaken with freshly prepared sodium hydrogen sulphite the bulk of the contained oil is converted into a mixture of crystalline additive compounds with the reagent, and these, after washing and draining, can be decomposed with aqueous potassium carbonate. The resulting oil consists almost wholly of aldehydes of the fatty series, mainly heptaldehyde; when shaken with aqueous hydroxylamine acetate it loses its characteristic odour and yields more than one-half its weight of crystals, which, after being drained and recrystallised once from methyl alcohol, form plates melting at about 53°. (Found, $C = 65.4$; $H = 12.0$. $C_7H_{14}{:}NOH$ requires $C = 65.1$; $H = 11.7$ per cent.)

The compound was compared with heptaldoxime (m. p. 53—55°) prepared from commercial œnanthol; the substances were identical in all respects.

For the further proof that the compound forming the bulk of the above oil is *n*-heptaldehyde its cyanohydrin was prepared from the crystalline hydrogen sulphite compound and hydrolysed. The resulting hydroxy-acid (m. p. 66—67°) on titration gave the equivalent 162 ($C_8H_{16}O_3$ requires 160) and direct comparison of the corresponding substance from commercial œnanthol afforded proof of its identity with α-hydroxy-*n*-octoic acid.

The oily residue left after passing steam through distilled gingerol, if dissolved in ether and then shaken with aqueous sodium hydrogen sulphite, frequently furnishes a small quantity of a solid hydrogen sulphite compound of a ketone; the bulk of this may remain dissolved in the aqueous layer, from which, as well as from the solid, the ketone can be recovered by adding a slight excess of hydrochloric acid, boiling off sulphur dioxide, and extracting with ether. In this way there is usually obtained a sweet-smelling oil with a very pungent taste.

The new ketone, for which the name "zingerone" is proposed, was not obtained in solid form until a highly purified synthetic specimen solidified; various specimens of the compound obtained from gingerol subsequently set to solid masses by infection.

In order to obtain supplies of the ketone from extract of ginger, the authors have since utilised the fact that gingerol is readily, in part, decomposed by hot baryta water into aldehydes mainly volatile in steam, and the new ketone. By boiling crude extracts of the drug with baryta water so long as the odour of œnanthol is perceptible in the distillate, acidifying the residue, extracting with ether, and subsequently dealing with the ethereal extract in the manner above indicated, the new ketone is conveniently and quickly obtained.

The yield of zingerone from gingerol is very much below that theoretically possible; this is doubtless due to the occurrence of polymerisation or secondary re-condensation of the sensitive products of hydrolysis.

Decomposition of Methylgingerol. Formation of Fatty Aldehydes and Methylzingerone.

Purified methylgingerol behaves towards hydrolytic agents and when heated alone in much the same way as does gingerol itself. The yields of the simpler products were in this case, however, more satisfactory, especially when boiling baryta water was used and the fatty aldehydes were removed with the steam as soon as formed.

Even from recrystallised methylgingerol the fatty aldehydes were of mixed character, and this is in agreement with the mixed nature of the fatty acids obtained on oxidation (p. 782). The ketonic product is in this instance not soluble in alkalis, has no perceptible

odour, and, as it is but very slightly volatile in steam, most of it remains in the flask after removal of fatty aldehydes. It is recovered by extraction with ether and is readily obtained in crystalline form. The properties of this compound, which is the monomethyl ether of zingerone, are described later.

Properties of the New Ketone, $C_{11}H_{14}O_3$.

The compound when pure is a colourless solid which dissolves somewhat freely in most of the usual organic media, with the exception of petroleum, and crystallises from ether in needles, rhombohedra, or large, lustrous plates melting at 31—34°. It has a distinct, sweet odour reminiscent of salicylaldehyde and to a less extent of vanillin. It has an extremely pungent taste like that of ginger itself, but quantitative comparisons have not yet been carried out.

When warmed with concentrated mineral acids, best with hydrobromic acid, it gives a striking colour reaction. The liquid, at first faintly yellow, passes through brownish-yellow, reddish-brown, to brown tints, then becomes opaque purple and blue in thin layers, and ultimately deep purple; on careful addition of alkali the colour becomes blue, then faintly green, or nearly colourless.

Zingerone is but slightly volatile in steam. As it was not obtained in crystalline form until the research was otherwise completed, no attempt was ever made to determine the composition of the product from gingerol by direct analysis. The formula was deduced from those of its solid and more easily purified derivatives. The substance dissolves only very sparingly in water, but freely in dilute aqueous sodium or potassium hydroxides, being reprecipitated by carbon dioxide. In alcoholic solutions, it gives a green coloration with ferric chloride. Its alkaline solutions give neutral, non-pungent, insoluble products when treated with benzoyl or sulphonyl chlorides, and with chlorocarbonic esters. These observations show that zingerone has a phenolic character. It is optically inactive in alcohol or benzene.

Zingerone also has the character of a ketone, and readily yields a crystalline phenylhydrazone (plates, m. p. about 143°) and semi-carbazone (needles, m. p. about 133°); but these, as well as other hydrazones and oximes, were found very difficult to purify as they quickly decomposed in solution.

The *ethylcarbonato*-derivative, $C_{11}H_{13}O_2 \cdot O \cdot CO_2Et$, was prepared by cautiously adding ethyl chloroformate to an ice-cold solution of the ketone in aqueous sodium hydroxide. The resulting solid was collected, dried, and crystallised from ether.

Found : C. 63·1, 63·2 ; H = 6·7, 6·7.

$C_{14}H_{18}O_5$ requires C = 63·2 ; H = 6·7 per cent.

It formed large, flat, calcite-like prisms melting at 45—47°.

The *methyl* derivative (methylzingerone), $C_{11}H_{13}O_2 \cdot OMe$, was pre-
pared by shaking an ice-cold solution of zingerone in aqueous
sodium hydroxide with methyl sulphate. It is also obtained, as has
already been mentioned, by heating or hydrolysing "methylgin-
gerol." It dissolves readily in most of the usual organic media
with the exception of petroleum ; it is insoluble in water or alkalis,
and crystallises from alcohol in colourless needles melting at
55·5—56·2°.

Found : C = 68·9 ; H = 7·7.

$C_{12}H_{16}O_3$ requires C. 69·2 ; H = 7·7 per cent.

The methyl derivative has no phenolic properties, but it gives
the same colour reactions with hydrochloric acid as does zingerone
itself. It displays ketonic characters, gives crystalline derivatives
with semicarbazide, phenylhydrazines, and hydroxylamine. It is
fully saturated, and does not reduce cold permanganate in acetone
solution or decolorise bromine in chloroform. When oxidised with
permanganate in dilute aqueous sulphuric acid it gives veratric
acid (m. p. 179° ; proof by mixed melting point method).

Methylzingeroneoxime, $C_{12}H_{16}O_2 \cdot NOH$, was prepared by warming
the foregoing compound in alcoholic solution with hydroxylamine
hydrochloride and excess of sodium acetate. It was isolated by
diluting with water and extracting with ether. It crystallises from
light petroleum or ether in slender needles melting at 91—92°.

Found : C = 65·0 ; H = 7·8 ; N = 6·7.

$C_{12}H_{17}O_3N$ requires C = 64·6 ; H = 7·6 ; N = 6·3 per cent.

When dissolved in a little pyridine and ether, treated with
bromine water in excess, and then with hydrogen peroxide
(Piloty's test for ketoximes) it gives a definite, although not very
intense, yellowish-green colour (bromonitroso-compound) which
passes into the ethereal layer.

Constitution of Methylzingerone and Zingerone.

As the sensitive phenolic hydroxyl group of zingerone is absent
in the methyl derivative, the latter was considered to be the most
suitable compound with which to begin experiments with the view
of throwing light on the structure of these substances.

Attempts to bring about the Beckmann change in the oxime were
not fruitful, but the oxidation of methylzingerone itself gave the
necessary clue.

When the methyl ether was warmed with aqueous sodium hypo-

bromite, the odour of bromoform soon became perceptible and the solid passed into solution. At the end of some hours' interaction, sodium sulphite in excess was added to destroy unchanged hypobromite, steam was passed through the solution to remove carbon tetrachloride and other impurities, then the acid products were liberated by addition of mineral acid and extracted with ether. The latter extracted a mixture which on repeated recrystallisation from ether was resolved into two main portions, one containing halogen and the other free from it. The latter formed plates, and when recrystallised from water was found to be hydrated, but after exposure in a vacuum became anhydrous and melted at 95—97°:

0·6573 Gram required 31·5 c.c. $N/10$-NaOH for neutralisation with phenolphthalein as indicator, whence the equivalent $=208$; that required for a monobasic acid, $C_{10}H_{13}O_2 \cdot CO_2H$, being 210.

The acid agreed in general characters with β 3 : 4-dimethoxy-

$$\text{MeO} \underset{(I)}{\overset{OMe}{\diamondsuit}} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \qquad \text{MeO} \underset{(II)}{\overset{OMe}{\diamondsuit}} \text{CO}_2\text{H}.$$
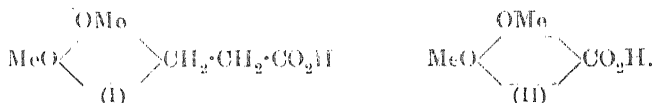
phenylpropionic acid (I) and this inference appeared to be more probable as gingerol had yielded protocatechuic acid and methylgingerol, veratric acid (II). It was clear that methyl zingerone must be the methyl ketone of the acid, or

$$C_{10}H_{13}O_2 \cdot CO \cdot CH_3,$$
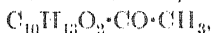
and therefore probably

$$\text{MeO} \overset{OMe}{\diamondsuit} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3.$$
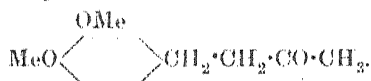
Synthetic experiments, described in Part II., have established the truth of this inference. Moreover, a synthesis of zingerone itself, which is described in the same communication, has shown that of the two alternative formula deducible from that of the methyl ether, the formula

$$\text{HO} \overset{OMe}{\diamondsuit} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3.$$
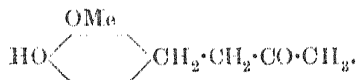
must be assigned to zingerone; the latter is therefore 4-hydroxy-3-methoxyphenylethyl methyl ketone.

The Constitution of Gingerol.

There is no reason to doubt that, except for the numbers of carbon atoms contained in the residues which furnish the fatty aldehydes on hydrolysis, the structure of the two or more pungent constituents of gingerol are essentially similar, and therefore,

mutatis mutandis, the following remarks are applicable to all such constituents. The molecule of that component of gingerol which furnishes heptaldehyde clearly has the composition of a compound of that aldehyde with zingerone, that is, $C_7H_{14}O + C_{10}H_{10}(OMe)\cdot OH$, methylgingerol being $C_7H_4O + C_{10}H_{10}(OMe)_2$. The ketonic character of these two compounds is not a matter reasonably admitting of doubt, but the function of the fourth oxygen atom is certainly not quite clear.

It is extremely difficult, if not impossible, to depict a condensation product of one molecule of heptaldehyde with one of methylzingerone which accords with the above conclusions, without assuming that the fourth oxygen atom has hydroxylic functions. The only reasonable alternative would appear to involve one of the following assumptions: (1) that the carbonyl groups in the ketone and the aldehyde are jointly engaged in the grouping

$$>C<_O^O>C< \; ;$$
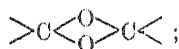
but this is not in accordance with the ready hydrolysis of gingerol and methylgingerol with baryta water, as such complexes are normally stable to alkalis; or (2) that the molecule contains a peroxide-like grouping, such as:

$$\begin{array}{ccc} O-O & & O----O \\ | \;\; | & \text{or} & | \qquad | \\ -C-C- & & -C\cdot CH_2\cdot C- \\ | \;\; | & & | \qquad | \end{array}\; ;$$
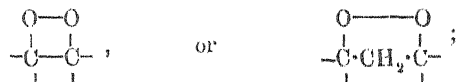
but the two substances have none of the characters of peroxides. Again, neither of these assumptions is in harmony with the fact that methylgingerol reacts with hydroxylamine, giving a ketoxime which yields unchanged methylgingerol once more by mild hydrolysis.

The authors have been forced to infer, therefore, that the fourth oxygen atom has hydroxylic functions, and that the failure of methylgingerol to give methane with magnesium methyl iodide is due to the primary reaction of the reagent with the carbonyl group and the insolubility of the additive product; the reaction of methylgingerol with acetyl chloride, and more especially with phenylcarbamide, are fully in agreement with this view.

If the presence of the hydroxyl group in methylgingerol is assumed, then this compound and gingerol itself appear as "aldols," and the whole of their properties, including the optical activity, with one signal difficulty, are readily understood, and the pungent constituents of gingerol can be represented by one of the two general formulæ:

$$CH_3 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH(OH) \cdot [CH_2]_n \cdot CH_3$$

OMe

OH

or

$$CH_2 \cdot CH \Big\langle \begin{matrix} CH(OH) \cdot [CH_2]_n \cdot CH_3 \\ CO \cdot CH_3 \end{matrix},$$

OMe

OH
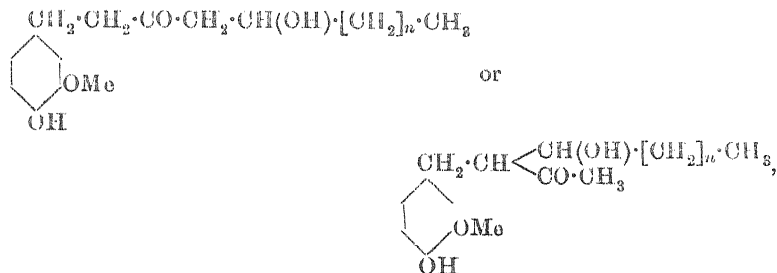
where the residue $C_x H_{2x+1}$ is a saturated alkyl radicle, probably normal in all cases, and $n = 5$ and either 4 or 3 (or both). Having regard to the very general occurrence in natural products of open, straight-chain, aliphatic residues, the first of the two general formulæ appears the more probable. The optical activity of the compounds is explicable on the basis of either of the formulæ suggested.

Summary.

The oleo-resin, gingerol, the pungent principle of *Zingiber officinale*, which was first investigated by Thresh and more recently by Garnett and Grier, is essentially a mixture of optically active saturated phenolic compounds derived from a residue of zingerone, or 4-hydroxy-3-methoxyphenylethyl methyl ketone, in association with a molecular proportion of the residue of a saturated aliphatic aldehyde, which in the main constituent is *n*-heptaldehyde. The constituents are probably "aldols" (β-hydroxy-ketones) of the general type:

$$C_6 H_3 (OH)(OMe) \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH(OH) \cdot [CH_2]_n \cdot CH_3,$$

where n in the principal constituent is 5, and 4, or possibly 3, in the main secondary constituent.

Only traces of solid matter, of camphoraceous appearance, have been observed in gingerol, but methylgingerol, a mixture of the monomethyl ethers of the gingerol constituents, and methylgingerol oxime, has been obtained in crystalline form.

extraction of the drug, and to the British Pharmaceutical Confer
ence for the use of a grant from which part of the expenses of the
research was defrayed.

LXVI.—The Pungent Principles of Ginger. Part II. Synthetic Preparations of Zingerone, Methyl-zingerone and Some Related Acids.

By ARTHUR LAPWORTH and FREDERICK HENRY WYKES.

IN Part I. evidence was adduced that the phenolic ketone,
"zingerone," obtained from gingerol, the pungent oleo-resin of
ginger, was 4-hydroxy-3-methoxyphenylethyl methyl ketone (I) or
a position isomeride, and that "methylzingerone," the correspond-
ing ketone from "methylgingerol," is its methyl ether, (II), 3:4-
dimethoxyphenylethyl methyl ketone.

$$CH_2 \cdot CH_2 \cdot CO \cdot CH_3 \qquad\qquad CH_2 \cdot CH_2 \cdot CO \cdot CH_3$$

OMe   OMe
OH   OMe

(I.)   (II.)
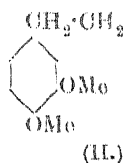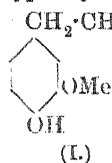
The authors have prepared these, and also several important
acids that were required for purposes of comparison, by synthetic
methods, which in certain cases represent the first direct syntheses
of the compounds in question and in other cases are simpler or
give better yields than previous methods.

The synthesis of methylzingerone presented no difficulty, as
3:4-dimethoxystyryl methyl ketone (II), from veratraldehyde and
acetone, is easily made in good yield and is readily reduced by
sodium amalgam, giving 3:4-dimethoxyphenylethyl methyl ketone,
which is identical with methylzingerone (II).

$$CH:CH \cdot CO \cdot CH_3 \qquad CHO \qquad CH:CH \cdot CO \cdot CH_3$$

OMe   OMe   OMe
OMe   OH   OH

(III.)   (IV.)   (V.)
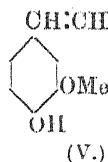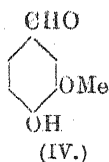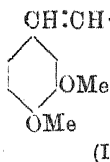
A similar process for preparing 4-hydroxy-3-methoxyphenylethyl
methyl ketone by condensing vanillin (IV) with acetone and
reducing the resulting 4-hydroxy-3-methoxystyryl methyl ketone
(V) gave very poor yields at each stage, but the final product was

identical with zingerone. On the other hand, good yields were quickly obtained by the following process.

Vanillin (V) gives an excellent yield of ethyl vanillylideneacetoacetate (VI) by Knoevenagel and Albert's method (*Ber.*, 1904, **37**, 4476); this unsaturated ester was easily reduced by means of sodium amalgam, and the product with excess of alkali was converted into an acid, doubtless *vanillylacetoacetic acid* (VII), which when heated lost the elements of carbon dioxide and was converted into zingerone (V).

CH:CAc:CO₂Et   CH₂·CHAc·CO₂H   CH:CAc₂

$$\text{CH:CAc:CO}_2\text{Et} \qquad \text{CH}_2\text{·CHAc·CO}_2\text{H} \qquad \text{CH:CAc}_2$$

OMe   OMe   OMe

OH   OH   OH

(VI.)   (VII.)   (VIII.)
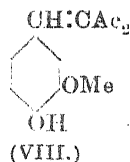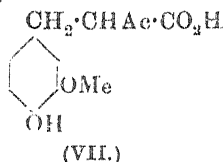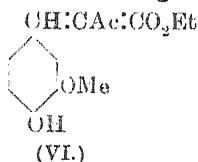
Synthetic zingerone was obtained in crystalline form, and had the characteristic sweet odour and pungent taste of the ketone from the decomposition of gingerol. The solid when used to infect samples of ketone obtained from the drug caused these to solidify for the first time. The properties of the synthetic ketone were identical in every respect with those of the compound from ginger.

An attempt to imitate this synthesis through vanillylideneacetylacetone (VIII) was not successful, and the reduction products of the latter compound were not of the type expected.

The authors' work included some simple direct syntheses of hydroferulic acid (XI) and of hydrocaffeic acid (XIII). These have previously been obtained by the reduction of synthetic ferulic and caffeic acids (Tiemann and Nagai, *Ber.*, 1878, **11**, 650, 672) prepared by the Perkin "cinnamic acid synthesis." As the authors' methods, although obvious enough, are new, if not in principle, and are very easily carried out, the steps may be indicated.

Vanillin (V) was condensed with diethyl malonate or ethyl cyanoacetate, yielding diethyl vanillylidenemalonate and ethyl vanillylidenecyanoacetate (IX) respectively. These were readily reduced at the double bond, and on subsequent hydrolysis with excess of alkali were converted into acids, doubtless vanillylmalonic acid (X) in both instances. The product when heated yielded hydroferulic acid (XI).

$$\text{CH:C(CN)·CO}_2\text{Et} \qquad \text{CH}_2\text{·CH(CO}_2\text{H)}_2 \qquad \text{CH}_2\text{·CH}_2\text{·CO}_2\text{H}$$

OMe   OMe   OMe

OH   OH   OH

(IX.)   (X.)   (XI.)
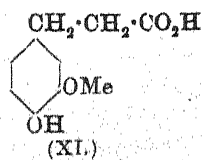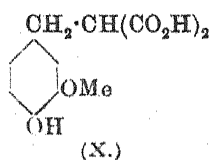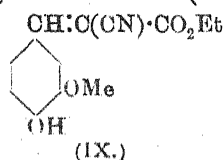
A precisely analogous process, applied to protocatechualdehyde instead of vanillin, gave hydrocaffeic acid (XIII) through the intermediate condensation product (XII).

$$CH:C(CN)\cdot CO_2Et$$

$$CH_2\cdot CH_2\cdot CO_2H$$

(XII.)   (XIII.)
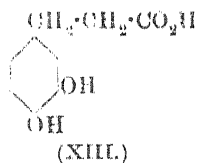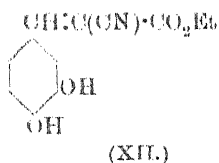
It is worthy of remark that all the unsaturated phenolic ketones and esters (I, V, VIII, IX, and XII) give solutions in alkali which in the thinnest layers exhibit an intense yellow colour that disappears on reduction at the double bond. The effect is perhaps most pronounced with (XII), which exhibits with boric acid a reaction very like that associated with curcumin, the colouring matter of turmeric. The constitution which Kostanecki suggests for curcumin is

$$CH:CH\cdot CO\cdot CH_2\cdot CO\cdot CH:CH$$
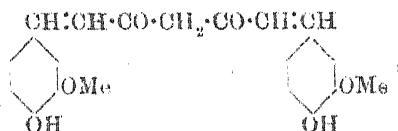
in which case it is obviously very closely related to the similar compounds dealt with in the present paper.

The question of the groupings essential to the pungency of gingerol, zingerone, and similar compounds is one which one of us is hopeful of reserving for a short time. So far, it would appear certain that the presence of the free phenolic hydroxyl group is essential, and also, not improbably, the ketonic carbonyl suitably disposed in a saturated chain attached to the phenolic residue.

EXPERIMENTAL.

I. *Synthesis of Zingerone (4-Hydroxy-3-methoxyphenylethyl Methyl Ketone).*

Preparation of Ethylcarbonatovanillin,

OMe

$$CO_2Et\cdot O\langle\qquad\rangle CHO .$$

As vanillin and its acetyl and benzoyl derivatives did not readily condense with acetone, the ethylcarbonato-derivative, which is new, was prepared by adding one molecular proportion of ethyl chloroformate to vanillin dissolved in the requisite quantity of *N*-sodium

hydroxide. The derivative separated in the cold in small, white needles, and after an hour was collected and crystallised from hot alcohol.

Found: $C = 63.3$; $H = 5.9$.

$C_{11}H_{12}O_4$ requires $C = 63.5$; $H = 5.8$ per cent.

The substance crystallises from alcohol in slender needles and melts at $65°$. It is slowly hydrolysed by cold dilute alkali. When it was dissolved in excess of acetone and the mixture treated with a little dilute sodium hydroxide, an intense yellow colour was produced, and apparently a small quantity of the desired condensation product was formed, as the neutral product of the reaction, when reduced with sodium amalgam, gave an oily mixture which had a pronounced pungent taste. The authors have not yet had opportunities to follow up these observations.

Reduction of Vanillylidene Derivatives of Acetylacetone and Ethyl Acetoacetate. Formation of Zingerone.

Vanillylideneacetylacetone, which was prepared by Knoevenagel and Albert's method (*Ber.*, 1904, **37**, 4480), forms an intensely yellow solution in sodium hydroxide; this colour is discharged by shaking the solution with sodium amalgam, and on saturating the resulting liquid with carbon dioxide, an oil, doubtless *vanillyl-acetylacetone*, $HO \cdot C_6H_3(OMe) \cdot CH_2 \cdot CH(CO \cdot CH_3)_2$, is deposited and ultimately tends to crystallise; as the oil when heated with acid or alkaline hydrolytic agents gave no product with the characters of vanillylacetone, its further investigation was not undertaken.

Ethyl vanillylideneacetoacetate, which was also obtained in nearly theoretical yield by Knoevenagel and Albert's method (*loc. cit.*, p. 4476), crystallised in pale yellow needles melting at 112.5—$113.5°$, and as Knoevenagel and Albert give the melting point as 120—$121°$, the authors analysed their product. (Found, $C = 63.3$; $H = 6.0$. $C_{14}H_{16}O_5$ requires $C = 63.5$; $H = 6.1$ per cent.)

The ester was dissolved in 10 per cent. aqueous sodium hydroxide and the intensely yellow solution shaken violently with washed, fluid, sodium amalgam, the whole being kept very cool. When the solution no longer displayed a yellow colour in thin layers, it was separated from mercury, mixed with 35 per cent. of its weight of solid sodium hydroxide, and heated for about eight hours on the water-bath, when it was cooled, saturated with carbon dioxide, and extracted with ether to remove unhydrolysed *ethyl vanillyl-acetoacetate*, $OMe \cdot C_6H_3(OH) \cdot CH_2 \cdot CHAc \cdot CO_2Et$, an oily compound which represents the first stage in the reduction process.

The aqueous residue was next acidified and extracted with ether, the latter then being dried and evaporated. The oily extract was heated in a vacuum, when at first carbon dioxide was evolved, and the residual material distilled at 175—210°/15 mm.

In order to separate the products, the distillate was dissolved in aqueous sodium hydroxide, which was then saturated with carbon dioxide and extracted with ether ("phenolic extract"), the aqueous residue being subsequently acidified with hydrochloric acid and again extracted with ether ("acidic extract").

The "phenolic extract" when dried and evaporated left a brown oil. This was dissolved in N-sodium hydroxide solution and treated in the cold with ethyl chloroformate, when the bulk of the material in solution was converted into an oil which solidified on scratching the vessel with a glass rod. The solid was dissolved in ether, the solution dried, and allowed to evaporate spontaneously. Large, tabular crystals were deposited, which on recrystallisation from light petroleum formed colourless, hexagonal plates melting at 47·5°.

Found: $C = 62·7$; $H = 6·7$.

$C_{14}H_{18}O_5$ requires $C = 63·1$; $H = 6·8$ per cent.

The substance was identical in all respects with the ethylcarbonato-derivative of the ketone ("zingerone") obtained from gingerol.

In order to obtain the free phenolic ketone, the foregoing compound was heated on the water-bath with dilute aqueous sodium hydroxide until a homogeneous liquid resulted. Excess of hydrochloric acid was then added and the cooled product extracted with ether. After drying and evaporating, the ethereal extract left a residue, which was distilled in a vacuum, when the distillate set to a crystalline mass.

The solid material, obtained as above, was purified by dissolving it in dry ether, adding enough petroleum to cause a turbidity, allowing the latter to settle, and then infecting the clear solution with a trace of solid 4-hydroxy-3-methoxyphenylethyl methyl ketone. On spontaneous evaporation, the liquid deposited lustrous, flat, colourless crystals which had the odour of the above ketone and melted at 36—37°.

Found: $C = 67·7$; $H = 7·2$.

$C_{11}H_{14}O_3$ requires $C = 68·0$; $H = 7·3$ per cent.

4-Hydroxy-3-methoxyphenylethyl methyl ketone obtained in this way had an extremely pungent taste and was in every respect identical in properties with "zingerone." As has already been mentioned, the "zingerone" from the natural source was not

obtained in crystalline condition until infected with a trace of the synthetic ketone, which had solidified spontaneously after distillation in a vacuum.

4-Hydroxy-3-methoxyphenylethyl methyl ketone is not the only product which is formed by reduction of ethyl vanillylideneacetoacetate and subsequent hydrolysis. The "acidic extract" (compare p. 794) gave on evaporation a small quantity of an acid which was moderately soluble in cold water and readily so in hot; this formed colourless leaflets melting at 133—134°, and was at first believed to be hydrocaffeic acid, which also crystallises in leaflets and melts at 137—139°. The substance obtained as above, however, unlike hydrocaffeic acid, gives no coloration with ferric chloride, and when it is mixed with hydrocaffeic acid the mixture melts at 127—132°. A titration with alkali, using phenolphthalein as indicator, gave an equivalent for this acid of about 240; the quantity of this material obtained in the pure state was, however, too small to permit of further investigation.

Oxidation and Reduction of 3:4-*Dimethoxystyryl Methyl Ketone. Formation of Dimethylcaffeic Acid and of Methylzingerone.*

3:4-Dimethoxystyryl methyl ketone was prepared by condensing veratraldehyde with acetone (compare Francesconi and Cusmano, *Gazzetta*, 1908, **38**, ii, 70 *et seq.*) and purifying it by recrystallisation from light petroleum. (Found: C = 70·0; H = 6·8. $C_{12}H_{14}O_3$ requires C = 69·9; H = 6·8 per cent.)

The compound crystallises from carbon tetrachloride in microscopic leaflets. When it is warmed with concentrated hydrochloric acid, it gives a deep red coloration, doubtless due to the intermediate formation of veratraldehyde, which gives a similar reaction.

3:4-Dimethoxystyryl methyl ketone is readily oxidised when shaken with aqueous sodium hypobromite, being converted into dimethylcaffeic acid, $C_6H_3(OMe)_2 \cdot CH\!:\!CH \cdot CO_2H$, which was isolated in small, flat needles (from water) melting at 180—181°.

Reduction of 3:4-dimethoxystyryl methyl ketone with the aid of Paal and Skita's or Willstätter's methods did not proceed in a very satisfactory manner, but when an alcoholic solution of the compound was shaken with liquid sodium amalgam, the bright yellow colour rapidly lost its intensity, and when this process was carried out in presence of excess of potassium hydrogen carbonate, good yields of the desired reduction product were obtained. It was isolated by diluting the aqueous-alcoholic solution with water, extracting with ether, and shaking the ethereal extract with

freshly prepared sodium hydrogen sulphite solution. The solid
hydrogen sulphite compound was collected, washed with ether,
dried, and then decomposed by warming it with excess of aqueous
sodium carbonate. By extracting the resulting liquid with ether,
3 : 4-dimethoxyphenylethyl methyl ketone was obtained in quantity
corresponding with about 80 per cent. of that theoretically possible.
It was purified by crystallisation from methyl alcohol.

Found: $C = 69\cdot4$; $H = 7\cdot8$.

$C_{12}H_{16}O_3$ requires $C = 69\cdot2$; $H = 7\cdot7$ per cent.

The substance formed colourless, odourless needles melting at
55—56°, and its identity with "methylzingerone," obtained by
methylating "zingerone" or by the decomposition of "methyl-
gingerol," was established by the usual methods. Its colour
reactions with hydrochloric acid and the properties of its oxime
(long, white needles, m. p. 92°) were indistinguishable from those
of the corresponding compounds obtained from "gingerol."

III. *Synthesis of Hydroferulic Acid.*
Ethyl Vanillylidenecyanoacetate,

$$HO\overset{\text{OMe}}{\underset{}{\diagup}}\diagdown CH\text{:}C(CN)\cdot CO_2Et\ .$$
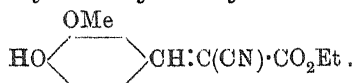
Vanillin and ethyl cyanoacetate were mixed in molecular pro-
portions and heated on the water-bath until a homogeneous liquid
was obtained, when a few drops of piperidine were added and
the heating was continued until a test portion solidified com-
pletely. Alcohol (twice the weight of vanillin present) was added,
and the whole allowed to cool. The crystals obtained were washed
with dilute hydrochloric acid, dried, and crystallised from alcohol.
With material obtained from mother liquors, the total yield of
condensation product approached that theoretically possible.

Found: $C = 62\cdot2$; $H = 5\cdot3$.

$C_{13}H_{13}O_4N$ requires $C = 63\cdot1$; $H = 5\cdot3$ per cent.

Ethyl vanillylidenecyanoacetate separates from alcohol in
yellow needles melting at 107°. It dissolves in aqueous sodium
hydroxide, giving a solution which shows an intensely yellow
colour even in thin layers; it is reprecipitated unchanged from
this solution on the addition of acids.

Formation of Hydroferulic Acid from Ethyl Vanillylidene-
cyanoacetate.

The reduction of ethyl vanillylidenecyanoacetate was accom-
plished by means of sodium amalgam in precisely the same manner

as was used for the reduction of ethyl vanillylideneacetoacetate (p. 793). The reduction product [mainly, no doubt, a mixture of vanillylcyanoacetic acid, $HO \cdot C_6H_3(OMe) \cdot CH_2 \cdot CH(CN) \cdot CO_2H$, and its ethyl ester] was heated with excess of potassium hydroxide until the ester present had been completely hydrolysed, when excess of acid was added and the liquid extracted with ether. The latter was evaporated and the residue heated in a vacuum to expel carbon dioxide; the hydroferulic acid left was purified by converting it into its lead salt, which is very sparingly soluble in water, and decomposing the latter in aqueous suspension with hydrogen sulphide.

Hydroferulic acid, obtained in the above way, crystallises from hot water in stout, white needles melting at 89—90°. It dissolves readily in hot water, less readily in cold, and only sparingly in concentrated hydrochloric acid. Its aqueous solution gives no coloration with ferric chloride. (Found: $C = 60\cdot6$; $H = 6\cdot2$. $C_{10}H_{12}O_4$ requires $C = 60\cdot6$; $H = 6\cdot1$ per cent.) The acid agreed very closely in properties with those assigned by Tiemann and Nagai (*Ber.*, 1878, **11**, 650) to the acid obtained by the reduction of ferulic acid.

Diethyl vanillylidenemalonate, $HO \cdot C_6H_5(OMe) \cdot CH\!:\!C(CO_2Et)_2$, was prepared from vanillin and ethyl malonate by Knoevenagel and Albert's method (*loc. cit.*, p. 4481). It had the properties ascribed to it by these authors.

On reduction with sodium amalgam and subsequent treatment in the manner described in the case of ethyl vanillylidenecyanoacetate, it yields hydroferulic acid.

IV. *Synthesis of Hydrocaffeic Acid.*

Hydrocaffeic acid was prepared by Tiemann and Nagai (*Ber.*, 1878, **11**, 672) by the reduction of synthetic caffeic acid. The following is a simple alternative synthesis.

Condensation of Protocatechualdehyde with Ethyl Cyanoacetate. Formation of Ethyl α-Cyanocaffeate,
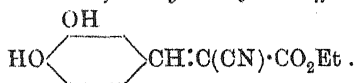
This condensation was effected by means very similar to those used in similar condensations in previous sections, but it was found desirable to dilute the mixture of aldehyde and ester with a little absolute alcohol. The product, which was contaminated

with a brown impurity, was purified by extraction with benzene and recrystallisation therefrom.

Found: C = 61·6; H = 4·9.

$C_{12}H_{11}O_4N$ requires C = 61·8; H = 4·7 per cent.

Ethyl α-cyanocaffeate is a yellow, microcrystalline solid which melts somewhat indefinitely at 162—166°, and dissolves in alkali to give an intensely orange solution. A test-paper made by dipping paper in an alcoholic solution of this ester behaves towards boric acid in much the same way as does turmeric paper, that is, if moistened with boric acid solution and then heated it turns brown, but the temperature required is somewhat higher than with turmeric.

Formation of Hydrocaffeic Acid from Ethyl α-Cyanocaffeate.

A solution of ethyl α-cyanocaffeate in alkali was reduced with sodium amalgam until colourless. The resulting liquid, which very quickly turned brown on exposure to air, was made strongly alkaline by the addition of solid sodium hydroxide, boiled for two days under a reflux condenser, cooled, acidified, and extracted with ether. The ethereal extract gave an oil which soon deposited crystals; these were not isolated, but the whole was heated to expel carbon dioxide, then dissolved in water, treated with animal charcoal, and allowed to crystallise. The crystals of hydrocaffeic acid obtained in this way were hexagonal leaflets melting at 138—139°, were moderately soluble in cold water, readily so in hot, and their aqueous solution gave a green colour with ferric chloride, changing to a rich purple on the addition of ammonia. These properties correspond closely with those assigned to hydrocaffeic acid by Tiemann and Nagai (*loc. cit.*).

The authors have also found that hydrocaffeic acid is readily obtained from hydroferulic acid by heating it with dilute hydrochloric acid (about 5 per cent.) at 200° for six hours in a closed tube.

LXVII.—*The Determination of Ozone and Oxides of Nitrogen in the Atmosphere.*

By FRANCIS LAWRY USHER and BASRUR SANJIVA RAO.

THE investigation recorded in this paper arose from the observation, common to residents in tropical climates, that rubber articles and cotton and silk fabrics perish, and certain colouring matters are bleached, far more rapidly than in temperate latitudes. The explanation which at first seems natural, namely, that increased temperature or increased intensity of light, or both of these, may be chiefly responsible for the observed effects, appears to be inadequate because, although the factors named undoubtedly contribute to the deterioration of certain articles exposed to their influence, this deterioration is well marked in the case of articles kept in comparative darkness. An alternative hypothesis is that the atmosphere in the tropics contains some chemically destructive substance which is either absent from, or present in far smaller quantity in, the atmosphere of higher latitudes. This hypothesis obviously suggests ozone as the substance postulated, and it receives support from the well-known observations that tropical sunlight exceeds both in quantity and in actinic power that of temperate climates, and that ozone is a product of the action of ultra-violet light on oxygen. We have been unable to discover any satisfactory record of experiments on the amount of ozone in the atmosphere in the tropics, and since the question is one of considerable practical importance as well as of scientific interest, the problem has been attacked experimentally in Bangalore. The experiments so far carried out do not support the hypothesis, but at present they are too few to permit any definite conclusion being drawn. The object of the present paper is to show that the methods of estimation hitherto practised are probably untrustworthy, and to describe a new method which we believe to be free from their defects. This method is applicable to the estimation of ozone, nitrogen peroxide, and, in certain cases, of hydrogen peroxide.

Previous Work.

Much work has been done on the methods of estimating ozone and on the application of those methods to the analysis of the atmosphere; a useful summary of it is given in a paper on the subject by Hayhurst and Pring (T., 1910, **97**, 868). Besides the work cited in that paper, we may mention that of Keiser and McMaster (*Amer. Chem. J.*, 1908, **39**, 96), who used a solution of permanganate to distinguish between ozone, hydrogen peroxide, and nitrogen per-

oxide. According to these authors, air when passed through permanganate solution is deprived of hydrogen peroxide and nitrogen peroxide, and any ozone which it may contain, being unaffected by the permanganate, can be estimated by one of the usual methods. On the other hand, if the air is passed over powdered manganese dioxide, both ozone and hydrogen peroxide are destroyed and the nitrogen peroxide may be estimated. Finally, passage through chromic acid serves to distinguish between ozone and hydrogen peroxide, of which it destroys only the latter.

Rothmund and Burgstaller (*Monatsh.*, 1913, **34**, 75) showed that, in the estimation of ozone and hydrogen peroxide, potassium iodide is untrustworthy on account of secondary reactions, but pointed out that satisfactory results could be obtained by substituting the bromide in acid solution for the iodide, and by subsequently adding iodide and titrating the liberated iodine. This process is, however, unsuited to the estimation of ozone in exceedingly small concentrations.

Value of Previous Determinations of Ozone.

Before describing a new method, it is desirable to state the grounds on which the older methods are held to be objectionable. In the absence of a generally accepted standard method, the objections are necessarily incapable of direct proof, but are none the less valid. In some instances, the results obtained by different methods under the same conditions of time and place are mutually contradictory, but usually no such check is available, and in that case the experiments may be open to criticism on physical and chemical grounds. Objections on physical grounds are best exemplified in the method adopted by Hayhurst and Pring (*loc. cit.*), and subsequently used in a slightly modified form by Pring (*Proc. Roy. Soc.*, 1914, [*A*], **90**, 204). Here the air to be examined was blown across the surface of a liquid reagent contained in a shallow vessel, the efficiency of the arrangement having been tested by passing the gases from an ozoniser, mixed with excess of air, through two such vessels at the rate of 6 litres per minute, and considered satisfactory because "all the ozone was taken up in the first vessel, and no appreciable liberation of iodine occurred in the second." The only conclusion that can justifiably be drawn from this experiment is that the greater part of the ozone in a mixture which was presumably far richer in that gas than is atmospheric air was absorbed in the first vessel, whereas the only important question, how much ozone escaped absorption, is left unanswered. Chemists who have been concerned with the removal of minute traces of a gas by a liquid absorbent will have difficulty in assuming that ozone present

to the maximum extent of, say, 1 part in 200,000 parts of air can have been quantitatively absorbed under such conditions, for it is the last traces of the absorbable gas that are so difficult to remove from a mixture. The foregoing criticism is probably applicable, although not in so marked a degree, to all estimations of ozone where the current of air has not been finely subdivided, either by passage over a closely packed solid reagent or mechanically before passage through a liquid reagent.

Unless the error introduced by inefficient absorption is large compared with the quantity to be measured, it is important only in those experiments which claim to have a quantitative significance; whereas if they are objectionable on chemical grounds even their qualitative value may be questioned. We venture to suggest that all the recorded determinations based on the direct use of potassium iodide are untrustworthy for the following reasons, in addition to those stated by Rothmund and Burgstaller (*loc. cit.*). (1) The liberated iodine is appreciably volatile in the current of air, even when fairly concentrated potassium iodide is used; (2) when iodate is formed, the reaction between the iodic and hydriodic acids which occurs when the liquid is acidified is very slow at great dilutions; (3) any nitrous acid present is reduced to nitric oxide, which then combines with dissolved oxygen and furnishes more iodine; (4) solutions of potassium iodide are unstable in the presence of air, even in the dark. It is true that the difficulties under the first three heads might be surmounted, but the oxidation of a neutral iodide solution by air in the dark is bound to occur unless some suitable negative catalyst can be found, and must vitiate the results of any experiment in which a long time elapses between its commencement and the final titration. Most previous workers who have examined the stability of potassium iodide solutions agree that iodine is liberated by the combined action of air and light, and that in the presence of acids—even of so weak an acid as carbonic—oxidation may take place in darkness, but it has been found that carefully purified iodide * also furnishes iodine in the dark, as is seen from the following figures (p. 802), which relate to solutions kept in darkness for two days in the presence of air freed from oxidising impurities.

The error introduced in this way is certainly small if an experiment is of short duration, but in some of those carried out by Hayhurst and Pring nearly three weeks elapsed before the solution was titrated. Even when determinations are carried through

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* Ordinary "pure" potassium iodide appears always to contain free alkali, as well as iodate, and it is possible that the presence of the former accounts for the negative results obtained by some. The iodide used in our own experiments was treated with aluminium amalgam to reduce the iodate, and was recrystallised from alcohol to remove the alkali.

Experi-ment.	Solution in contact with	C.c. N/1000-thiosulphate equivalent to iodine liberated	
		as free iodine.	as iodate.
I.	Purified air containing carbon dioxide	1·55	nil.
II.	Purified air free from carbon dioxide	1·30	0·4
III.	Same as in II. ; more concentrated solution...	1·40	0·7

rapidly, however, the unavoidable errors due to secondary reactions, demonstrated by Rothmund and Burgstaller, remain. The substitution of cadmium potassium iodide for potassium iodide, recommended by Baskerville and Crozier (*J. Amer. Chem. Soc.*, 1912, **34**, 1332), does not seem likely to eliminate those errors, the only advantage claimed for the cadmium salt being that it is more stable to light and to certain impurities.

The method proposed by Keiser and McMaster (*loc. cit.*) is open to several objections. In the first place, ozone will not pass unchanged through permanganate solution unless nitrogen peroxide and hydrogen peroxide are absent, for both these substances reduce the permanganate to a manganous salt, which is known to be attacked by ozone. Moreover, the speed of the reaction between nitrous acid and ozone in aqueous solution is comparable with that of the reaction between nitrous acid and permanganate, so that a considerable proportion of the ozone must be destroyed during its passage through the solution, and the amount of nitrous acid found must be too low. Finally, the actual estimation of ozone was carried out by the potassium iodide method.

EXPERIMENTAL.

The initial difficulty lay in securing the quantitative removal of the very minute traces of ozone and oxides of nitrogen present in air, for which purpose probably the only effective apparatus is that devised by Reiset and described in Hempel's "Methods of Gas Analysis." By using this contrivance it would have been possible to deal with very large quantities of air, and to attain a corresponding accuracy; but there is one serious objection to such a procedure, namely, the risk of decomposing the ozone catalytically during its passage through the fine perforations in the platinum disks. This risk would probably be serious even if glass disks were used in place of platinum, for it is known that ozone is decomposed by contact with broken glass. The alternative method is to shake the reagent with a known volume of air in a closed vessel, but if this is done the maximum quantity of air that can be conveniently

dealt with is about 7 litres, which may be expected to contain not more than 0·02 milligram of ozone. This is just ten times the quantity that can be detected by any process involving a titration of iodine, and since no other titration process is so sensitive it was necessary either to sacrifice accuracy or to employ a more sensitive method. After prolonged trial of various processes—chiefly modifications of Rothmund and Burgstaller's—we finally adopted the one which will now be described. Its trustworthiness and accuracy will be discussed later.

In principle the method is extremely simple, and depends on the reaction between ozone and alkali nitrite in aqueous solution, a reaction which we have found to take place quantitatively according to the equation :

$$O_3 + NaNO_2 = O_2 + NaNO_3.$$
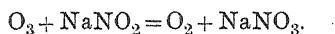
Two samples of air are taken and collected in 7-litre stoppered bottles. One sample is admitted through two tubes containing respectively chromic acid and powdered manganese dioxide, and the other through a tube containing chromic acid only. The samples thus collected are shaken with a dilute standard solution of sodium nitrite made slightly alkaline, and the nitrite content of the bottles is subsequently determined colorimetrically by the Griess–Ilosvay method (production of red dye with α-naphthylamine and sulphanilic acid ; see Sutton's " Volumetric Analysis," 9th ed., p. 449). The first sample of air contains only nitrogen peroxide, the ozone and hydrogen peroxide having been destroyed, and the increase in the quantity of nitrite in the bottle is equivalent to the nitrogen peroxide absorbed. The second sample contains ozone and nitrogen peroxide, and the difference between the quantities of nitrite in the two bottles after shaking is equivalent to the ozone present. The particulars of the procedure at present adopted are as follows, and since the success of the method depends on the care observed in attention to small details, these will be dealt with rather fully.

The vessels used for collecting the air are 5-kilogram " ammonia " bottles with glass stoppers, and have a capacity of about 7 litres. They are cleaned thoroughly with chromic acid mixture, washed with purified water, and afterwards left for several days full of ozonised air to remove all traces of oxidisable matter. The stoppers must fit accurately and be free from grease. The samples of air are collected over water, and it is necessary that the latter should be quite free from dissolved impurities, particularly nitrous acid. We prepare a large quantity of distilled water of suitable purity and keep it in a stock bottle protected from the atmosphere, the same water being used repeatedly, and tested at frequent

intervals. The manner of filling the bottles with air is important, the following method having been found the most satisfactory.

The bottle (*A*) is first filled completely with purified water, and a rubber stopper is then pushed into the neck. This stopper carries two tubes, of which one (*B*) admits air, whilst the other (*C*) serves as an exit for the water. The tube (*C*) is about 30 cm. long and of 3 mm. bore, and projects only 1 or 2 mm. inside the stopper, the other end being provided with a tap. (*B*) is of capillary bore, and
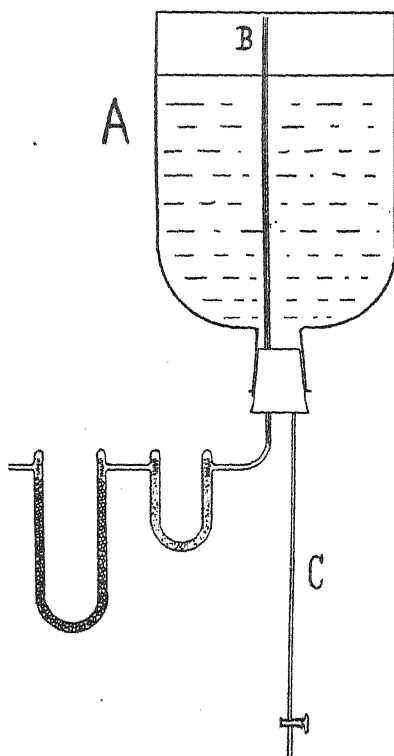
passes to the bottom of the bottle. Outside the stopper it is sealed to the tube or tubes containing the chromic acid and manganese dioxide: only sealed glass junctions are permissible in this system of tubes. On inverting the whole apparatus and opening the tap, the bottle fills with air, the volume of which is equal to that of the water that escapes. The object of this arrangement is, of course, to avoid bubbling the air through water, which might deprive it of part of the ozone and oxides of nitrogen. The tap is regulated so that air enters at the rate of about 1 litre per minute.

The chromic acid tube has a bore of 1 cm., and may be either straight or U-shaped. It is filled with glass beads coated with purified solid chromic acid, and for safety these beads should occupy 30 cm. of the tube. Chromic acid purchased as "pure" has been found to contain traces of nitric acid, and contaminates air passed over it with nitrogen peroxide. The reagent is therefore prepared by precipitating barium chromate, washing this thoroughly with water, and then digesting it with moderately dilute sulphuric acid, free from nitric acid. The solution of chromic acid thus obtained is treated with sufficient baryta water to remove any sulphuric acid, and is then concentrated on a water-bath until it becomes pasty. At this stage the glass beads are stirred into it, and are then introduced into the tube that is to be used, and dried in a current of air at 100°.

The manganese dioxide is mixed with asbestos wool that has been well washed and ignited, and the mixture is packed into a tube which may safely be one-half the length of the chromic acid tube. It is necessary to test the manganese dioxide, since some specimens contain traces of alkali or of manganous oxide, and may take up small amounts of nitrogen peroxide.

When the samples of air have been collected the rubber stoppers are withdrawn and immediately replaced by the glass ones. The latter are then lifted just sufficiently to admit the point of a pipette, and the following liquids are introduced: (1) 25 c.c. of $N/40,000$-sodium nitrite, made up with $N/1000$-sodium hydroxide in place of water; (2) 100 c.c. of pure water. The water used in these experiments must, of course, be proved free from nitrous acid or any other impurity that could affect the result, and the sodium hydroxide must be prepared from metallic sodium and purified water, since the solid as purchased always contains traces of nitrite. After the introduction of the liquid, the stoppers are secured and the bottles shaken for at least half an hour on a shaking machine. The contents of each separately are then made up to 250 c.c. These solutions are examined separately in the following way. Fifty c.c. are mixed with 5 c.c. of the Griess–Ilosvay reagent in a small stoppered flask, which is then kept in a water-bath at 75° for ten minutes. At the same time 50 c.c. of a standard sodium nitrite solution ($N/400,000$) is treated in exactly the same way. The solutions are then placed in the observation tubes of a Duboscq colorimeter and their strengths compared. Readings are taken for eight different positions of the tubes.

A simple formula can be obtained for calculating the results:

let $V =$ c.c. of air collected through chromic acid,

$\quad\quad r =$ ratio of length of column of standard solution to that of column of experimental solution.

Then the volume concentration of nitrogen peroxide will be 1 in $V/0\cdot014(r-1)$ of air. And if

$V' =$ c.c. of air collected through chromic acid and manganese dioxide,

$r' =$ ratio of length of column of standard solution to that of column of experimental solution,

the volume concentration of ozone will be 1 in $1/0\cdot007(r/V - r'/V')$ of air, assuming that nitrite solutions of the strengths given above are used.

It is, of course, possible to estimate hydrogen peroxide in addition to ozone and nitrogen peroxide, by collecting a third sample of air which has not been passed over any reagent, and treating it in exactly the same way as the other samples,[*] but probably this determination would be unsatisfactory in any place where the air was not exceptionally "pure," especially if traces of sulphur dioxide or hydrogen sulphide were present.

Critical Examination of the Foregoing Method.

Since it is claimed that the process just described is more trustworthy than those previously used for the determination of ozone and oxides of nitrogen in the atmosphere, and should replace them, it will be well to state the grounds on which that claim is based. To give full experimental details would make this paper inordinately long; we shall therefore mention only the results of a number of experiments which have been made to test various possible sources of error.

In the first place, the reaction on which the method is based is complete even at very great dilutions. This was proved by shaking a small quantity of exceedingly dilute nitrite solution for half an hour with air containing, in one case, a slight excess of ozone, and in the other a slight deficiency; it was impossible afterwards to detect nitrite in the first or ozone in the second. The nature of the reaction could not be investigated at very great dilution owing to the absence of a standard method by which to check the estimation of ozone, but it was elucidated in the case of ozone concentrations between 0·01 and 0·08 per cent. by the application of the potassium bromide method. Two bottles were filled simultaneously, through a T-tube, with feebly ozonised air, and the percentage of

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* It has been found that hydrogen peroxide does not oxidise nitrite in alkaline or neutral solution, but does so rapidly in acid solution. In estimating hydrogen peroxide it is therefore necessary to acidify the liquid. This must be done just before addition of the Griess–Ilosvay reagent.

ozone in it was determined by the nitrite and bromide methods respectively. Four experiments gave the following results:

	I.	II.	III.	IV.
Nitrite method	0·0263	0·0136	0·0124	0·0802 per cent.
Bromide method ...	0·0254	0·0127	0·0124	0·0800 „

The calculations were made on the assumption that one molecule of ozone reacted with one of sodium nitrite, and the satisfactory agreement shown by the figures proves that assumption to be justified. The following facts were established by further experiments.

(1) When purified air is shaken with water or an aqueous solution for one hour, no detectable quantity of ozone is produced.

(2) Ozone at a great dilution is not appreciably destroyed when shaken with water for one hour.

(3) Hydrogen peroxide present as vapour in air is completely destroyed * by passage of the air, at a rate not exceeding 1 litre per minute, through a chromic acid tube prepared as described above.

(4) Ozone is completely destroyed by passage through a tube containing asbestos-wool mixed with manganese dioxide.

(5) Ozone is not affected by passage over chromic acid.

(6) Nitrogen peroxide is not absorbed from air containing it by solid chromic acid † or by manganese dioxide, provided the latter contains no alkali or manganous oxide.

(7) $N/400,000$-Sodium nitrite solution undergoes no alteration in strength by shaking for two hours with purified air.

(8) If air containing nitrogen peroxide is passed through a tube of manganese dioxide (a) alone, and (b) with ozone, the amount of nitrogen peroxide recovered is in each case the same as that which was introduced.

Effect of Impurities.

The presence in air of traces of ammonia, sulphur dioxide, and hydrogen sulphide does not interfere with the estimation of ozone and nitrogen peroxide, since all three gases are completely absorbed during passage through the chromic acid tube. Air charged with small quantities of these impurities was passed through the chromic acid tube and afterwards shaken with a sensitive reagent, and in no case was the latter affected. Nessler's reagent was used for detecting ammonia, dilute permanganate for sulphur dioxide, and an alkaline lead solution for hydrogen sulphide. It is difficult to say whether traces of ammonia would affect the esti-

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* By "completely destroyed" we mean that the quantity of substance remaining was undetectable by the most delicate tests.

† Even chromic acid solution absorbs nitrogen peroxide with great difficulty. In one experiment several hours' shaking was necessary before it became impossible to detect nitrogen peroxide in the residual air.

mation of hydrogen peroxide, but the other two gases would certainly invalidate it. For this reason we attach no importance to the nitrite process for the determination of hydrogen peroxide, although it might be used in places far removed from towns and railways, where sulphur compounds can be shown to be absent. In this connexion we would point out that the estimation, and even the detection, of hydrogen peroxide in the atmosphere presents great difficulties. Hitherto titanium sulphate has been used for the purpose, but since nitrous acid immediately destroys the yellow colour produced in that reagent by hydrogen peroxide, and ozone does so less readily, it is clear that the absence of a coloration does not prove the absence of hydrogen peroxide, although the production of the colour would be a qualitative proof of its presence.

Other impurities likely to be present in air are probably without any effect on the process. Chlorine or hydrochloric acid would make the estimation of nitrogen peroxide impossible, but would not affect that of ozone.

Accuracy.

The accuracy of the determination is limited by that of the final comparison of colours, provided the experimental solutions are "developed" by the Griess–Ilosvay reagent always under the same conditions. In order to find the degree of accuracy obtainable, two equal quantities of the same nitrite solution were "developed" and compared. The mean ratio of the lengths of the columns of liquid given by eight readings was 1·012 instead of the correct value, 1·000. This error corresponds with 1 part of ozone (or nitrogen peroxide) in 25 millions, and is therefore unimportant, for a difference of this order of magnitude possesses no interest. A source of error was certainly present in our own experiments, in the changing of the stoppers of the bottles containing the samples of air, and in lifting them for the purpose of introducing liquid. The amount of diffusion that could take place in two seconds through the neck of a bottle of 7 litres' capacity must, however, be very small, and the remedy is obvious, although we were unfortunately not able to apply it.

Results of Determinations.

Hitherto only fourteen complete determinations have been made, covering the period between July, 1916, and January, 1917. The results are interesting chiefly because on no occasion was any ozone found. Indeed, with two exceptions, no one of the three substances looked for was found in a quantity exceeding 1 in 20 millions. On November 18th, and again on the 22nd, nitrogen peroxide was present to the extent of 1 part in 5 millions and 1 in

4 millions respectively, the weather having been thundery, with very little rain, during the preceding week. The twelve negative results show, more clearly than argument, the trustworthiness of the process adopted, in the sense that in spite of its delicacy (the Griess–Ilosvay reagent used in the way we have described is sensitive to 1 part of nitrogen peroxide in 56 millions of air) it is possible with care to obtain concordant results.

The interpretation of the results may well be deferred until a much greater number, covering a longer period, are available. We may remark, however, that there is some ground for the opinion that ozone and nitrogen peroxide never occur together in the atmosphere. It has been shown that, at moderate dilutions, ozone rapidly oxidises nitrogen peroxide, so that the latter substance cannot be detected, for example, in the air from an ozoniser, whereas nitric acid is found in water through which such air is passed (compare Chapman and Jones, T., 1911, **99**, 1813). If this oxidation takes place at the great dilutions in which ozone must be supposed to exist in the atmosphere, it not only helps to explain the surprisingly small quantities both of ozone and of nitrogen peroxide found, but may also be considered an important factor in the production of the nitric acid which is a normal constituent of air.

CENTRAL COLLEGE,
BANGALORE, S. INDIA.   [*Received, May 18th*, 1917.]

LXVIII.—*Compounds of Ferric Chloride with Ether and with Dibenzyl Sulphide.*

By AQUILA FORSTER, CHRISTOPHER COOPER, and GEORGE YARROW.

THE work described in this paper was brought to a close in August, 1914, and as an early return to these investigations does not seem probable, it is thought advisable to place on record such results as were obtained.

As examples of double compounds of metallic chlorides with ether may be quoted

$GlCl_2, 2(C_2H_5)_2O$ (Atterberg, *Ber.*, 1876, **9**, 856).

$AlBr_3, (C_2H_5)_2O$; $HgBr_2, 3(C_2H_5)_2O$; $SnBr_2, (C_2H_5)_2O$ (Nicklès, *Jahresber.*, 1861, 200).

$TiCl_4, (C_2H_5)_2O$ (Bedson, *Journ. Chem. Soc.*, 1876, i, 311).

In the following work, a double compound of ferric chloride and ether has been isolated and its properties have been examined.

It has been found to combine with ammonia and with organic amines, forming insoluble, unstable complexes.

A double compound of ferric chloride with benzyl sulphide has also been isolated. With benzyl chloride it forms tribenzyl-sulphinium chloride ferrichloride, a compound prepared by Hofmann and Ott (*Ber.*, 1907, **40**, 430) by the condensation of benzyl sulphide, benzyl chloride, and ferric chloride. By means of these reactions, tribenzylsulphinium cyanide ferrichloride has been prepared, from which the free salt, tribenzylsulphinium cyanide, has been isolated.

<div align="center">EXPERIMENTAL.</div>

Ether Ferric Chloride.

Ten grams of anhydrous ferric chloride were added gradually to an excess of pure dry ether. The ferric chloride dissolved with the evolution of much heat, and during addition the mixture was cooled. The solution was placed in a desiccator, the excess of ether distilled off under diminished pressure, and the residue dried on a porous plate in a vacuum for several days. The product was a dark red, highly deliquescent solid, soluble in benzene, alcohol, or water:

0·6390 gave 0·2305 Fe_2O_3 and 1·1293 AgCl. Fe = 25·2; Cl = 44·02.

$C_4H_{10}O,FeCl_3$ requires Fe = 23·7; Cl = 45·0 per cent.

In boiling benzene solution no chlorination was observed. Alcohol and water immediately decompose the compound into ferric chloride and ether.

Action of Heat on Ether Ferric Chloride.

At 100° ether ferric chloride slowly decomposes with the evolution of ethyl chloride. This decomposition takes place quantitatively at higher temperatures over the free flame, pure ethyl chloride being obtained according to the equation:

$$(C_2H_5)_2O,FeCl_3 = 2C_2H_5Cl + FeOCl.$$
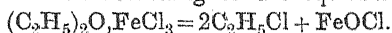
The ethyl chloride burnt with the characteristic green flame and gave a precipitate of silver chloride with a solution of silver nitrate in nitric acid. The gas was condensed in tubes in a freezing mixture, and the weight obtained corresponded closely with the loss in weight of the ether ferric chloride in agreement with the above equation. The liquid ethyl chloride boiled at 12—13° and its vapour density was found to be 35·5 (calc., 32·2). In one experiment 19·5 grams of the compound lost, on heating, 10·1 grams, or 52 per cent., whilst the theoretical loss, according to the

above equation, is 54 per cent. The ethyl chloride collected weighed 9·5 grams.

The Action of Ammonia on Ether Ferric Chloride.

On passing dry ammonia gas into a solution of ether ferric chloride in cold ether or benzene, a brick-red, amorphous powder separated. This was non-hygroscopic, insoluble in organic solvents, and was immediately decomposed with water or alcohol. With water, some samples dissolved, whereas others deposited ferric hydroxide, with solution of ammonium chloride. An analysis showed that the ammonia absorbed varied indefinitely from one to five molecules per molecule of ether ferric chloride, and a product of definite composition was not prepared, although no doubt this could be effected by the use of solutions of ammonia in place of ammonia gas. On destructive distillation, these substances gave ammonia and ethylamines, etc.

Aniline forms a double compound with ether ferric chloride which separates in dark brown plates, decomposing at 90° before melting.

Compounds of Ferric Chloride and Benzyl Sulphide.

Benzyl Sulphide Ferric Chloride.—Molecular proportions of benzyl sulphide and ferric chloride were dissolved in the minimum amounts of ether, and the well-cooled solutions were mixed. The mixture was allowed to remain for several hours, during which an evolution of heat was evident, and a brownish-yellow mass separated. The product, after filtration and washing with dry ether, was obtained as lemon-yellow, minute crystals, rapidly becoming brown on contact with the moist atmosphere. It is soluble in chloroform, sparingly so in alcohol, and insoluble in ether or acetone. It was purified by crystallisation from hot anhydrous alcohol or chloroform, and melted at 94°:

$0·3371$ gave $0·0711$ Fe_2O_3. $Fe = 14·90$.

$(C_7H_7)_2S,FeCl_3$ requires $Fe = 14·87$ per cent.

Benzyl sulphide ferric chloride is distinguished from tribenzyl-sulphinium chloride ferrichloride, which it resembles, by only a slight colour change when brought into contact with water. On remaining for some hours under water, it completely dissociates into benzyl sulphide and ferric chloride. Alkalis at once dissociate benzyl sulphide ferric chloride, forming benzyl sulphide and ferric hydroxide.

Condensation of Benzyl Sulphide Ferric Chloride with Benzyl
. Chloride.

The readiness with which benzyl sulphide and benzyl chloride combine to form tribenzylsulphinium chloride in the presence of ferric chloride is probably due to the intermediate formation of benzyl sulphide ferric chloride. This view is supported by the ready condensation of benzyl sulphide ferric chloride with benzyl chloride.

Benzyl sulphide ferric chloride (10·3 grams: 1 mol.) dissolved in 50 c.c. of chloroform was added to a solution of 4 grams (1 mol.) of benzyl chloride in chloroform. The mixture remained in a closed vessel overnight, and was then allowed to evaporate. Yellow needles were obtained, and identified as tribenzylsulphinium chloride ferrichloride (m. p. 98·5°).

Benzyl sulphide ferric chloride does not condense with ethylene dibromide, with bromoacetic acid, or with benzyl alcohol. In agreement with this is the singular fact that benzyl sulphide does not form sulphinium derivatives with these compounds when brought together in ethereal solution with ferric chloride; in each case only benzyl sulphide ferric chloride was obtained.

Decomposition of Benzyl Sulphide with Ferric Chloride.

When benzyl sulphide or dibenzyl disulphide and ferric chloride in molecular proportions were heated together at 100° for two to three hours, tribenzylsulphinium chloride ferrichloride (m. p. 98·5°) in approximately one-half molecular equivalent was formed. The filtrate, after washing the product with dry ether, was found to contain much ferrous iron, but no iron sulphide, and its contents, proving to be of a complicated nature, were not further identified.

Similarly, dibenzyl disulphide, benzyl chloride, and ferric chloride in molecular proportions in ether do not give a hexabenzyldisulphinium chloride derivative, but tribenzylsulphinium chloride ferrichloride, together with the decomposition products mentioned above. This decomposition of dibenzyl disulphide is in agreement with its well-known hydrolysis with alkalis into benzyl mercaptan and the complex decomposition products of benzyl sulphydroxide.

Action of Ammonia on Tribenzylsulphinium Chloride Ferrichloride.

Ammonia gas is absorbed by a solution of tribenzylsulphinium chloride ferrichloride, and an insoluble, brown, amorphous solid is formed, melting at 80—85°. It was unstable towards water, and analyses indicated three equivalents of ammonia per molecule, but they were not completed. Aniline and tribenzylsulphinium chloride ferrichloride combine in chloroform solution to form insoluble, yellowish-green plates, which decompose before melting.

Tribenzylsulphinium Chloride.

No means were found for the preparation of tribenzylsulphinium chloride in a state of purity. It was obtained from tribenzylsulphinium chloride ferrichloride by removal of the ferric chloride with alkalis as a viscous oil, which, contrary to former statements, was found but sparingly soluble in cold water. It appeared indifferent to solutions of mineral salts, and no double decomposition reactions were obtained. The rapid dissociation of tribenzylsulphinium chloride into benzyl sulphide and benzyl chloride was very apparent; it takes place in contact with water and is complete in three to four hours, and benzyl sulphide is generally to be found as a by-product of the reactions of its derivatives. The oil obtained as tribenzylsulphinium chloride doubtless contained benzyl sulphide and other products of decomposition.

Tribenzylsulphinium Cyanide Ferrichloride,
$(C_6H_5 \cdot CH_2)_3SCN,FeCl_3$.

Molecular proportions of benzyl sulphide and benzyl cyanide (phenylacetonitrile) were dissolved in dry ether and added to a well-cooled solution of ferric chloride in ether. The mixture was cooled and kept in a desiccator overnight, when a mass of crystals separated. They were collected, washed with ether, and obtained in lemon-yellow crystals melting at 76°, insoluble in ether, but soluble in alcohol or chloroform:

0·2091 gave 0·4103 CO_2 and 0·0812 H_2O.   C$=53·50$; H$=4·31$.
0·5301   „   0·01596 (gram) N_2.   N$=3·01$.
0·3163   „   0·0504 Fe_2O_3.   Fe $= 11·10$.
0·2800   „   0·1329 $BaSO_4$.   S$=6·52$.

$C_{22}H_{21}NS,FeCl_3$ requires C$=53·5$; H$=4·29$; N$=2·84$; Fe$=11·32$; S$=6·50$ per cent.

Tribenzylsulphinium cyanide ferrichloride was also prepared in

good yield by the condensation of benzyl sulphide ferric chloride and benzyl cyanide in molecular proportions in ethereal solution, and identified, by the mixed melting-point test, with the product described above.

On the addition of tribenzylsulphinium cyanide ferrichloride to water, only a slight colour change takes place, and no compound corresponding with the red bistribenzylsulphinium chloride ferrichloride, $[(C_6H_5 \cdot CH_2)_3SCl_2]_2,FeCl_3$ was obtained.

Tribenzylsulphinium Cyanide, $(C_6H_5 \cdot CH_2)_3SCN$.

To a warm solution of tribenzylsulphinium cyanide ferrichloride in alcohol was added an excess of ammonia solution (D 0·88). The precipitated ferric hydroxide was separated by filtration and tribenzylsulphinium cyanide crystallised from the filtrate. It forms large, white prisms melting at 41°, and is only sparingly soluble in water, but readily so in organic solvents:

0·1355 gave 0·3932 CO_2 and 0·0782 H_2O. C = 79·89; H = 6·41.

0·2105 „ 0·1492 $BaSO_4$. S = 9·74.

0·6506 „ 0·0288 (gram) N_2. N = 4·50.

$C_{22}H_{21}NS$ requires C = 79·76; H = 6·34; S = 9·67; N = 4·23 per cent.

Tribenzylsulphinium cyanide gave no double decomposition with mineral salts in solution. It condensed readily with ferric chloride in anhydrous solution, forming tribenzylsulphinium cyanide ferrichloride. A double compound of tribenzylsulphinium cyanide and platinum chloride was precipitated from an aqueous alcoholic solution in minute, sparingly soluble, red crystals melting at 162°:

0·6890 gave 0·1378 Pt. Pt = 20·0.

$C_{44}H_{42}S_2N_4PtCl_4$ requires Pt = 19·0 per cent.

The dissociation of tribenzylsulphinium cyanide in contact with water was complete in a few hours, benzyl sulphide and benzyl cyanide being formed. The reverse reaction, the direct combination of benzyl sulphide and benzyl cyanide, was not found to take place in twelve hours' heating on the water-bath. Hydrolytic agents invariably dissociated tribenzylsulphinium cyanide into benzyl sulphide and benzyl cyanide and its products, and no derivative of the original material could be prepared.

Preliminary experiments indicated that the reactions described also take place when mercuric chloride is used instead of ferric chloride, and it was proposed to examine the decomposition of benzyl sulphide and dibenzyl disulphide with this condensation agent.

ARMSTRONG COLLEGE,
NEWCASTLE-ON-TYNE.   *[Received, May 24th, 1917.]*

LXIX.—*The Effect of Additional Auxochromes on the Colour of Dyes. Part II. Triphenylmethane and Azo-dyes.*

By PRAPHULLA CHANDRA GHOSH and EDWIN ROY WATSON.

IN two previous papers from this laboratory (Medhi and Watson, T., 1915, **107**, 1581; Meek and Watson, T., 1916, **109**, 544) the effect of multiplying the auxochrome groups has been studied spectroscopically in the xanthene and anthraquinone groups of dyes. In the present paper the investigation has been extended to some azo- and triphenylmethane dyes, and some phenylfluorone dyes have been prepared, but have not yet been examined spectroscopically. The results here recorded have been obtained by observing with an ordinary spectroscope the positions of the edges of the absorption bands in solutions of different concentrations. Experience gained with the anthraquinone group has shown that it is much preferable to investigate the absorption spectra by means of a spectrophotometer, and it is hoped that the present work may subsequently be checked by the use of that instrument; but the results already obtained are now published, as it is unlikely that the authors will have further opportunity to study the subject together.

Little insight has yet been obtained into the mechanism by which additional auxochromes affect the absorption spectra. In fact, the effects produced are very different in different cases, and little explanation is as yet forthcoming as to why such varying effects should be produced. In some cases the multiplication of auxochromes produces the comparatively small effect of strengthening and broadening the absorption bands without much effect on their positions, as, for example, in the azobenzene series. In other cases the bands are shifted to a considerable extent, but remain of about the same breadth. In some cases the breadth is much affected; it may be either increased or diminished, whilst yet again in other cases additional bands appear. Even in the same series very diverse effects may be produced for no apparent reason. Apparently much more material is required before any explanation of the effects can be offered.

Absorption Spectra Examined.

Azo-group.

Aminoazobenzene	$C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot NH_2$	In dilute
Chrysoidine.................	$C_6H_5 \cdot N_2[1] \cdot C_6H_3(NH_2)_2[2:4]$	hydrochloric
4 : 4'-Diaminoazobenzene	$NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NH_2$	acid solution.

Benzeneazophenol	$C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot OH$	In dilute
Benzeneazoresorcinol ...	$C_6H_5 \cdot N_2[1] \cdot C_6H_3(OH)_2[2:4]$	potassium
Benzeneazoquinol	$C_6H_5 \cdot N_2[1] \cdot C_6H_3(OH)_2[2:5]$	hydroxide
Benzeneazocatechol	$C_6H_5 \cdot N_2[1] \cdot C_6H_3(OH)_2[3:4]$	solution.
Benzeneazopyrogallol ...	$C_6H_5 \cdot N_2[1] \cdot C_6H_2(OH)_3[2:3:4]$	

(Benzeneazo-α-naphthol..	$C_6H_5 \cdot N_2[1] \cdot C_{10}H_6 \cdot OH[4]$	
Absorption spectrum recorded by Tuck, T., 1909, **95**, 1809.)		In dilute
p-Hydroxybenzeneazo-α-naphthol	$OH \cdot C_6H_4 \cdot N_2[1] \cdot C_{10}H_6 \cdot OH[4]$	potassium
Benzeneazo-β-naphthol...	$C_6H_5 \cdot N_2[1] \cdot C_{10}H_6 \cdot OH[2]$	hydroxide
p-Hydroxybenzeneazo-β-naphthol	$OH \cdot C_6H_4 \cdot N_2[1] \cdot C_{10}H_6 \cdot OH[2]$	solution.

Benzeneazo-β-naphthyl-amine	$C_6H_5 \cdot N_2[1] \cdot C_{10}H_6 \cdot NH_2[2]$	In dilute hydrochloric
p-Hydroxybenzeneazo-β-naphthylamine	$OH \cdot C_6H_4 \cdot N_2[1] \cdot C_{10}H_6 \cdot NH_2[2]$	acid solution.

Benzeneazo-1:5-di-hydroxynaphthalene...	$C_6H_5 \cdot N_2[1] \cdot C_{10}H_5(OH)_2[4:8]$	
p-Hydroxybenzeneazo-1:5-dihydroxynaphth-alene......................	$OH \cdot C_6H_4 \cdot N_2[1] \cdot C_{10}H_5(OH)_2[4:8]$	In dilute potassium hydroxide solution.
p-Hydroxybenzeneazo-1:3-dihydroxynaphth-alene	$OH \cdot C_6H_4 \cdot N_2[1] \cdot C_{10}H_5(OH)_2[2:4]$	

The results are recorded in Figs. 1—6.*

It will be observed that the effect of adding a second amino-group to aminoazobenzene is slight. When the second amino-group is added to the same benzene nucleus, the front edge of the band (the edge nearer the red end of the spectrum) is shifted slightly towards the red; when the second amino-group is added to the other benzene nucleus, the edge of the band is shifted slightly towards the blue.

The effect of adding a second hydroxyl group to benzeneazo-phenol is similar. When the second hydroxyl group is added to the same benzene nucleus, the front edge of the band is shifted towards the red. Two additional hydroxyl groups in the same benzene nucleus produce the same general effect, namely, a shift of the front edge of the band towards the red. The shift is greatest in the case of benzeneazocatechol, then come benzeneazo-pyrogallol, benzeneazoquinol, and benzeneazoresorcinol in order,

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* Compare Tuck (T., 1907, **91**, 450) for absorption spectrum of benzene-azophenol; Hewitt and Thole (T., 1910, **97**, 513) for aminoazobenzene, and Hartley (T., 1887, **51**, 156) for chrysoidine.

according to the displacement produced. These results are in agreement with the generalisation already pointed out (Meek and Watson, *loc. cit.*, 558), that two hydroxyl groups in the *o*- or *p*-position with respect to one another give a deeper colour than

FIG. 1.

————————	*Aminoazobenzene*	*With* 20 *times the theoretical*
— — — —	*Chrysoidine*	*quantity of hydrochloric*
· · · · · · · · ·	4 : 4'-*Diaminoazobenzene*	*acid.*
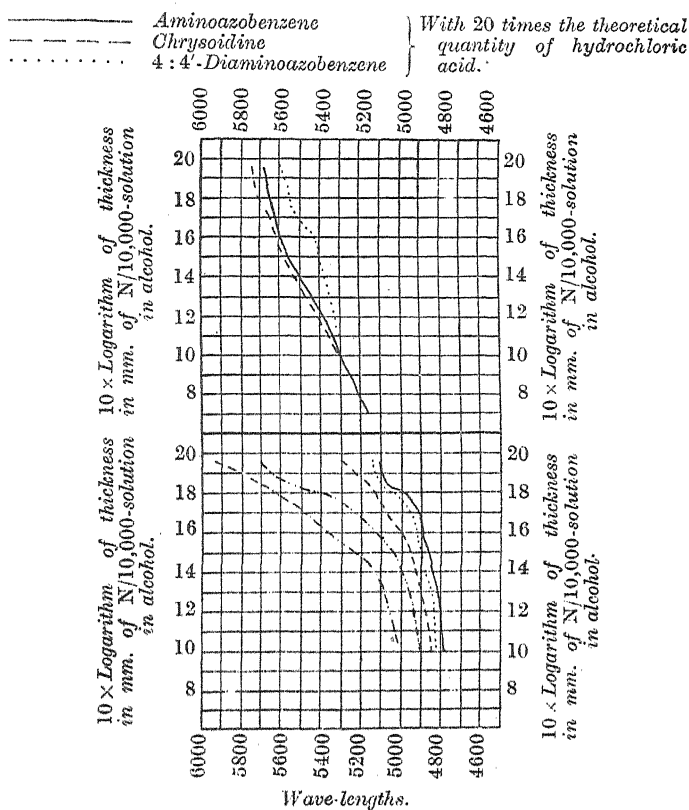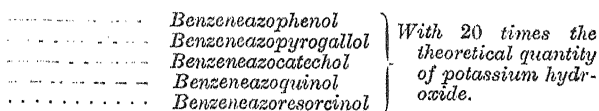
two hydroxyl groups in the *m*-position. The effect of two hydroxyl groups in the *o*-position with respect to one another is greater than that of three adjacent. (The blue colour of benzeneazo-quinol in potassium hydroxide is fugitive, and the absorption spectrum of this blue solution could not be observed.)

K K*

Hewitt (T., 1909, **95**, 1295) has recorded the absorption spectrum of aminobenzeneazophenol in dilute hydrochloric acid. Comparing it with that of aminoazobenzene, we see that in this case also the additional auxochrome has shifted the front edge of the band towards the red. Hewitt's observations extend into the ultra-violet, so that the effect of the additional auxochrome can be more completely described. Aminoazobenzene in dilute hydrochloric acid solution has two bands, one partly in the visible spectrum and the other completely in the ultra-violet. The additional auxochrome shifts both bands a little towards the red and increases their persistency.

FIG. 3.

Wave-lengths.
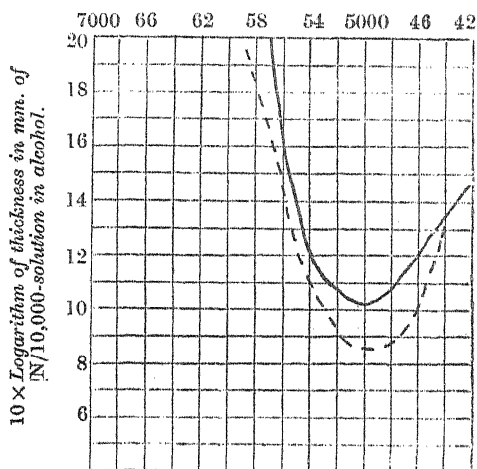
------------ *Benzeneazo-α-naphthol with sodium alkyloxide.* (Tuck.)
- - - - - p-*Hydroxybenzeneazo-α-naphthol with 20 times the theoretical quantity of potassium hydroxide.*

The addition of a hydroxyl group to the benzene nucleus of benzeneazo-α-naphthol produces only a slight increase in the persistency of the band, but if the extra group is added to the naphthalene nucleus in the *ana*-position with respect to the original hydroxyl group, the band is not only strengthened, but is shifted a long way towards the red. Two additional hydroxyl groups, one in the benzene nucleus and the other in the naphthalene nucleus in the *ana*-position with respect to the original hydroxyl group, have an additive effect, so that the band is shifted a little further than in the case of benzeneazo-1:5-dihydroxynaphthalene and is made still a little stronger. Two additional

hydroxyl groups, one in the benzene nucleus and the other in the
m-position with respect to the original hydroxyl group in the
naphthalene nucleus, produce scarcely any shift of the original
absorption band, but only a strengthening. This result is in
agreement with our previous experience that an auxochrome added
in the *m*-position with respect to one already present has very
little effect on the absorption.

Very different is the effect of the addition of a hydroxyl group
to the benzene nucleus of benzeneazo-β-naphthol, which not only

FIG. 4.

Wave-lengths.
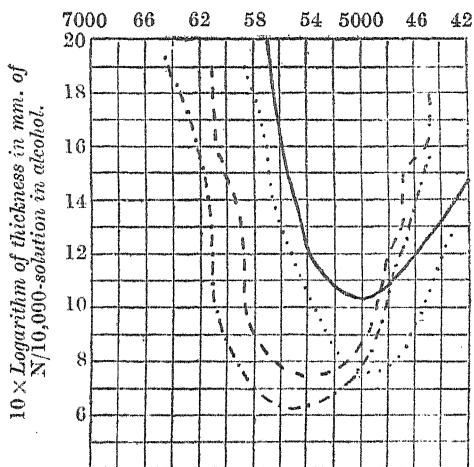
Benzeneazo-*a*-naphthol with sodium alkyloxide. (Tuck.)

— — — — — Benzeneazo-1 : 5-*dihydroxynaphthalene*
· — · — · — · p-*Hydroxybenzeneazo*-1 : 5-*dihydroxynaphthalene*
· · · · · · · p-*Hydroxybenzeneazo*-1 : 3-*dihydroxynaphthalene*

{ With 20 times
the theoretical
quantity of
*potassium
hydroxide.*

shifts the existing band further towards the red, but calls into
existence an entirely new band still further towards the red. In
the case of benzeneazo-β-naphthylamine, a similar addition also
seems to call into existence a new band, but apparently the already
existing band is shifted backwards, that is, towards the ultra-
violet. This may be because the additional auxochrome, that is,
the hydroxyl group, cannot exert its full effect in the acid solu-
tion. (It is, however, to be regretted that the absorption spec-
trum of benzeneazo-β-naphthylamine was not more completely
observed.)

K K* 2

Triphenylmethane Group.

Malachite-green ...	$C_6H_5 \cdot C(C_6H_4 \cdot NMe_2):C_6H_4:NMe_2Cl$	
4-Hydroxymala- chite-green	$OH \cdot C_6H_4 \cdot C(C_6H_4 \cdot NMe_2):C_6H_4:NMe_2Cl$	In dilute hydro- chloric
3:4-Dihydroxy- malachite-green	$(OH)_2C_6H_3 \cdot C(C_6H_4 \cdot NMe_2):C_6H_4:NMe_2Cl$	acid solution
2:3:4-Trihydroxy- malachite-green	$(OH)_3C_6H_2 \cdot C(C_6H_4 \cdot NMe_2):C_6H_4:NMe_2Cl$	
Aurin	$C(C_6H_4 \cdot OH)_2:C_6H_4:O$	
Resaurin............	$C([1]C_6H_3(OH)_2[2:4])_2:[1]C_6H_3(OH)[2]:O[4]$	In dilute potassium
Trihydroxyaurin (a)	$C([1]C_6H_3(OH)_2[3:4])_2:[1]C_6H_3(OH)[2]:O[4]$	hydroxide solution.
Trihydroxyaurin (b).................	$C([1]C_6H_3(OH)_2[2:5])_2:[1]C_6H_3(OH)[2]:O[4]$	

The results obtained by introducing hydroxyl groups into the phenyl group of malachite-green are very interesting. The band

Fig. 5.

Wave-lengths.

With 20 times the
theoretical quantity
of potassium
hydroxide.
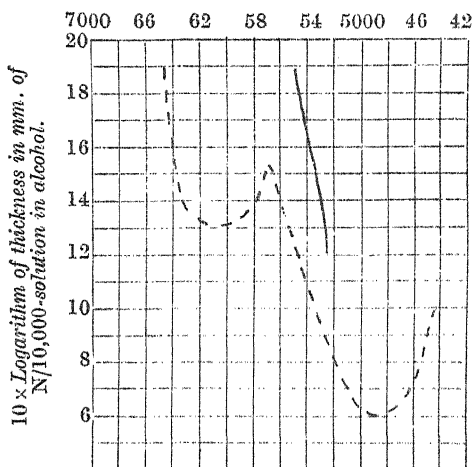
——————— Benzeneazo-β-naphthol
– – – – – p-Hydroxybenzeneazo-β-naphthol

of least frequency is shifted backwards, that is, towards the ultra-violet, whilst the next band is moved forwards from the ultra-violet into the visible part of the spectrum. Two hydroxyl groups in the *o*-position with respect to one another shift this second band further forwards than one hydroxyl group alone is able to do, whilst three adjacent hydroxyl groups produce an intermediate

effect (compare the effect of additional hydroxyl groups added to benzeneazophenol). These results fall into line with the effect produced by the addition of an amino-group to the unsubstituted benzene nucleus in Doebner's violet, when we pass to pararosaniline, or the similar addition of a dimethylamino-group to malachite-green, when we pass to hexamethylpararosaniline. In all these cases, the addition of auxochromes to the unsubstituted third benzene nucleus shifts the first band (the band of least frequency) backwards, so that the dye becomes lighter instead of deeper in colour. We see the same effect if we compare benzaurin (Meyer

FIG. 6.

Wave-lengths.

Benzeneazo-β-naphthylamine
p-Hydroxybenzeneazo-β-naphthylamine

With 20 *times the theoretical quantity of hydrochloric acid.*
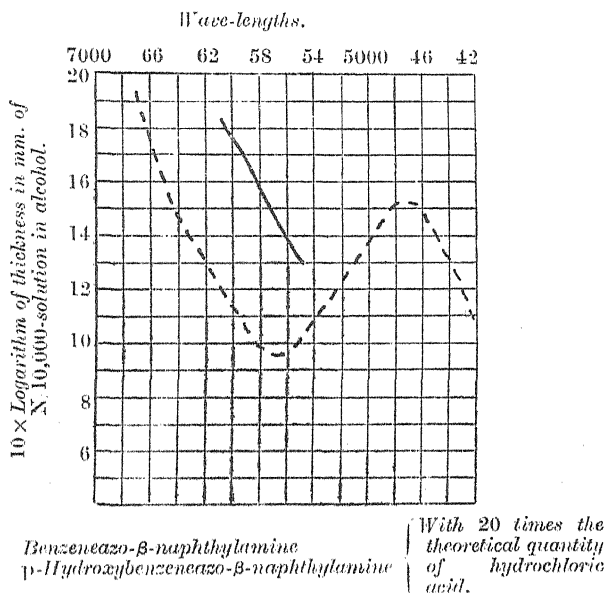
and Fischer, *Ber.*, 1913, **46**, 74) and aurin, so that it appears to be quite a general rule in the triphenylmethane group. It seems possible to explain this effect by means of the theory put forward by one of us (Watson and Meek, T., 1915, **107**, 1567) as to the nature of the vibrations causing the colour of dyes. In Doebner's violet, malachite-green, and benzaurin the vibration passes backwards and forwards through two of the benzene nuclei. In pararosaniline, hexamethylpararosaniline, and aurin the vibratory pulse, after passing through one benzene nucleus, finds two paths open to it, as each of the remaining nuclei is now capable of vibration. We may find a mechanical analogy by comparing the

transverse vibration of a string with that of a system of three strings, each of half its length, tied together at one point and all under the same tension, so that they make equal angles with one another.   Such a system will vibrate quicker than the simple string.   In the same way, when all three nuclei of the triphenyl-methane molecule are capable of vibrating, the period is less than when the vibration is confined to two of the nuclei.   In the latter case, the unsubstituted benzene nucleus may be compared to a dead weight at the centre of the simple string, which would make

FIG. 7.

Wave-lengths.

		Malachite-green		With 20 *times the*
		4-Hydroxymalachite-green		*theoretical quantity*
		3:4-Dihydroxymalachite-green		*of hydrochloric*
		2:3:4-Trihydroxymalachite-green		*acid.*
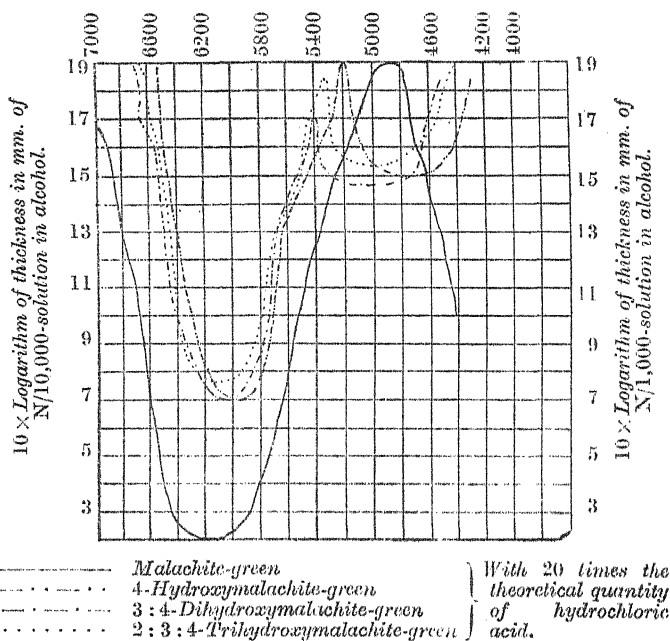
the vibration slower. By comparing Michler's hydrol and malachite-green, we see this effect.

Nothing can be said as to the cause of the second band in malachite-green and the hydroxymalachite-greens. It may be suggested that the first band of magenta, which is obviously com-pound, is produced by the fusion of the first and second bands of Doebner's violet, the second band having been brought further forward by the additional amino-group, which can exert its maxi-mum effect in dilute acid solution, than by the hydroxyl groups in the hydroxymalachite-greens, which could not exert their full

effect in acid solution. The same suggestion may be made as to the nature of the first band of aurin, which is also obviously compound.

With regard to the aurin derivatives examined, the series is not so complete as was desired. Pyrogallaurin could not be obtained by Caro's method (*Ber.*, 1892, **25**, 2678), and the alkaline solution of catecholaurin fades too rapidly to permit of the convenient examination of its absorption spectrum. Quinolaurin could not be prepared either by the condensation of formic acid and quinol or by Caro's method (*Ber.*, 1892, **25**, 1941) by the condensation of 3:6:3':6'-tetrahydroxydiphenyl-methane and quinol. In trihydroxyaurins (*a*) and (*b*) the band is shifted towards the red and becomes much narrower. As might have been expected, where there are hydroxyl groups in the *o*-position with respect to one another, the shift is greater than where they are para with respect to one another. In resaurin the band is shifted backwards. It may perhaps be suggested that in this compound fluorone condensation has occurred.

The Colour of Some Fluorone Dyes.

The following new compounds of this series have been prepared and their colours noted:

3 - *Dimethylamino*-9-p-*hydroxyphenyl*-6-*dimethylfluorime* — dyes dull red shades.

3-*Dimethylamino*-9-o-p-*dihydroxyphenyl*-6-*dimethylfluorime*—dyes red shades on chrome.

2 : 3 : 7-*Trihydroxy*-9-o-p-*dihydroxyphenyl*-6-*fluorone* — reddish-violet in potassium hydroxide solution; dyes reddish-violet shades on chrome.

1 : 3 : 8-*Trihydroxy*-9-o-p-*dihydroxyphenyl*-6-*fluorone*—orange in potassium hydroxide solution; dyes orange shades on chrome. Discussion of the colour is reserved until the absorption spectra have been examined.

Experimental.

p-*Hydroxybenzeneazo*-1 : 5-*dihydroxynaphthalene*, $OH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(OH)_2$.

An alcoholic solution of 1:5-dihydroxynaphthalene was mixed with a concentrated aqueous solution of *p*-hydroxybenzene-diazonium chloride, and then excess of sodium acetate was added. The precipitate was collected and washed thoroughly with water. The substance could not be crystallised, but was extracted with a mixture of benzene and alcohol. On concentrating the extract,

the pure dyestuff was deposited. It melts at 213—215°, and dyes reddish-violet shades on alum- or chrome-mordanted wool. Full dyeings are obtained with 2—3 per cent. of the dyestuff. The yield is almost theoretical:

0·1038 gave 8·8 c.c. N_2 at 25° and 763 mm. $N = 9·7$.

$C_{16}H_{12}O_3N_2$ requires $N = 10·0$ per cent.

p-*Hydroxybenzeneazo*-1 : 3-*dihydroxynaphthalene*, $OH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(OH)_2$.

p-Aminophenol hydrochloride was diazotised in the ordinary way and combined with an alkaline solution of 1 : 3-dihydroxy-naphthalene. The mixture was acidified after keeping overnight, and the precipitate was collected, washed with water, and dried. It could not be crystallised. It was purified by dissolving in alkali, precipitating with acid, and again dissolving in alcohol and precipitating with water. It does not melt below 300°:

0·1107 gave 10·2 c.c. N_2 at 29·2° and 763·5 mm. $N = 10·4$.

$C_{16}H_{12}O_3N_2$ requires $N = 10·0$ per cent.

p-*Hydroxybenzeneazo*-β-*naphthylamine*, $OH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

An alcoholic solution of β-naphthylamine was added to a concentrated aqueous solution of *p*-hydroxybenzenediazonium chloride. The precipitate was crystallised from alcohol, and melted at 156—157°:

0·0825 gave 11·4 c.c. N_2 at 27° and 762 mm. $N = 15·8$.

$C_{16}H_{13}ON_3$ requires $N = 15·97$ per cent.

The *hydrochloride* was deposited in crystalline form on adding hydrochloric acid to a hot alcoholic solution of the base and allowing the solution to cool. It melts at 170°.

o-*Aminobenzeneazo*-α-*naphthol*, $NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH$.

o-Nitrobenzeneazo-α-naphthol was obtained in a finely divided state by dissolving in cold concentrated sulphuric acid and precipitating with water. The precipitate was thoroughly washed free from acid, and was then warmed with a large volume (100 c.c. for 1 gram of the substance) of freshly prepared aqueous ammonium sulphide on the water-bath. After a few minutes, the whole of the azo-compound passed into solution. On remaining overnight, the solution deposited a fine, brown, shining precipitate, which was collected, well washed with water, and dried on a porous tile. The substance is very readily soluble in all ordinary solvents, and could not be crystallised. It was purified by extract-

ing with alcohol and precipitating with water. It melts at 195—196°:

0·0915 gave 13·2 c.c. N_2 at 32° and 761 mm. $N = 16·18$.

$C_{16}H_{13}ON_3$ requires $N = 15·97$ per cent.

$3 : 6 : 3' : 6'$-*Tetrahydroxydiphenylmethane*, $CH_2[C_6H_3(OH)_2]_2$.

According to Schorigin (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1094), this substance is brown. It was, however, obtained as a

FIG. 8.

Wave-lengths.

——————— Aurin	} With 20 times the
—·—·—·—· Resaurin	theoretical quantity
·—·—·—·— Trihydroxyaurin (a)	of potassium
············· Trihydroxyaurin (b)	hydroxide.
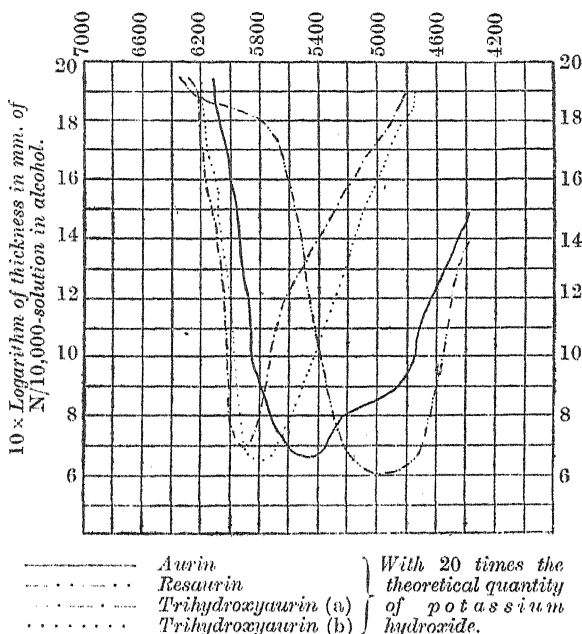
white, amorphous substance under the following conditions. Two and a-half grams of quinol were dissolved on gently warming with 25 c.c. of hydrochloric acid (1 : 10); 1 gram of 40 per cent. form-aldehyde solution was then added, and the mixture heated on the water-bath. The white precipitate of $3 : 6 : 3' : 6'$-tetrahydroxy-diphenylmethane began to appear in a minute, and the heating was continued for ten minutes. The compound could not be crystallised. It decomposes above 275°. (Found: $C = 66·68$; $H = 5·44$. $C_{13}H_{12}O_4$ requires $C = 67·2$; $H = 5·17$ per cent.)

Trihydroxyaurin (*b*),

$$C([1]C_6H_3(OH)_2[2:5])_2 \cdot [1]C_6H_3(OH)[2] \cdot O[4],$$
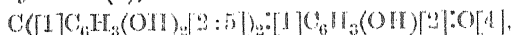
was prepared from $3:6:3':6'$-tetrahydroxydiphenylmethane and resorcinol by Caro's method (*Ber.*, 1892, **25**, 941). It could not be crystallised. It was purified by dissolving in alkali, precipitating with acid, and again dissolving in alcohol and precipitating with water. The operation was repeated twice to obtain the substance in a pure state. The yield was very low :

0·1020 gave 0·2633 CO_2 and 0·0413 H_2O. C = 70·41 ; H = 4·50.

$C_{19}H_{14}O_5$ requires C = 70·8 ; H = 4·34 per cent.

Trihydroxyaurin (*a*),

$$C([1]C_6H_3(OH)_2[3:4])_2 \cdot [1]C_6H_3(OH)[2] \cdot O[4],$$
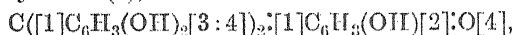
was prepared and purified in the same way as the above-mentioned trihydroxyaurin (*b*) :

0·1100 gave 0·2836 CO_2 and 0·0436 H_2O. C = 70·3 ; H = 4·4.

$C_{19}H_{14}O_5$ requires C = 70·8 ; H = 4·34 per cent.

4-Hydroxy-4′ : 4″-tetramethyldiaminotriphenylcarbinol Anhydride, or *4-Hydroxymalachite-green,* $O:C_6H_4:C(C_6H_4 \cdot NMe_2)_2$.

This dyestuff had already been obtained in a qualitative way by O. Fischer (*Ber.*, 1881, **14**, 2523), but not analysed. It was prepared by oxidising the leuco-compound in acetic acid solution with freshly precipitated manganese dioxide. The paste of manganese dioxide obtained from 0·52 gram of potassium permanganate was added to a solution of 1 gram of the leuco-compound in 35 c.c. of 30 per cent. acetic acid. The colour became dark green, and the mixture was warmed on the water-bath for an hour and filtered. The filtrate was treated with sodium acetate solution, whereby a violet precipitate of the dyestuff was obtained, which was crystallised from a mixture of benzene and toluene. The yield was good. It dyes mordanted wool in the following shades: blue on alum, bluish-violet on chrome, bluish-black on iron. Tannin-mordanted cotton is dyed to a dark violet shade :

0·1240 gave 8·8 c.c. N_2 at 33° and 763 mm. N = 7·98.

$C_{23}H_{24}ON_2$ requires N = 8·13 per cent.

2 : 4-Dihydroxy-4′ : 4″-tetramethyldiaminotriphenylcarbinol Anhydride, or *2 : 4-Dihydroxymalachite-green,* $O:C_6H_3(OH):C(C_6H_4 \cdot NMe_2)_2$.
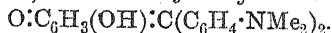
This dyestuff had already been obtained in a qualitative way by Votoček and Krauz (*Ber.*, 1909, **42**, 1605), but not analysed. It was prepared by oxidising a 30 per cent. acetic acid solution

of the leuco-compound with freshly precipitated manganese dioxide, and obtained as a fine blue solid which could not be crystallised. It dyes chrome-mordanted wool to a very brilliant blue shade:

0·1000 gave 7·1 c.c. N_2 at 33° and 762 mm. $N = 7·93$.

$C_{23}H_{24}O_2N_2$ requires $N = 7·77$ per cent.

3 : 6-*Tetramethyldiamino*-9-p-*hydroxyphenylxanthene*.

One gram of p-hydroxybenzaldehyde and 2 grams of m-dimethyl-aminophenol were dissolved in 50 per cent. aqueous alcohol, and 4 grams of concentrated sulphuric acid were then slowly added. The mixture was boiled under a reflux condenser for ten hours, and then the alcohol was expelled by boiling with water. The leuco-base was fractionally precipitated by sodium acetate, and the pure substance was obtained by crystallising the second fraction from dilute acetone. It melts at 220—221°:

0·0995 gave 6·8 c.c. N_2 at 32·5° and 762 mm. $N = 7·68$.

$C_{23}H_{24}O_2N_2$ requires $N = 7·77$ per cent.

The *benzoyl* derivative was prepared by the Schotten-Baumann reaction. It could not be crystallised because of its ready solubility in all common solvents. It melts and decomposes at 100—105°:

0·1500 gave 7·9 c.c. N_2 at 32° and 760 mm. $N = 5·89$.

$C_{30}H_{28}O_3N_2$ requires $N = 6·02$ per cent.

3-*Dimethylamino*-9-p-*hydroxyphenyl*-6-*dimethylfluorime* was prepared by oxidising the leuco-compound in acetic acid solution with freshly precipitated manganese dioxide. The dyestuff was precipitated from the acetic acid solution by aqueous sodium acetate solution, as it could not be crystallised. It dyes dull red shades:

0·1000 gave 7·0 c.c. N_2 at 33° and 762 mm. $N = 7·83$.

$C_{23}H_{22}O_2N_2$ requires $N = 7·77$ per cent.

3-*Dimethylamino*-9-o-p-*dihydroxyphenyl*-6-*dimethylfluorime*.

Two grams of 2 : 4-dihydroxybenzaldehyde and 4 grams of m-dimethylaminophenol were dissolved in 50 per cent. aqueous alcohol, and 8 grams of sulphuric acid (D 1·84) were then gradually added. The mixture was heated under a reflux condenser for twenty-four hours and filtered. The filtrate was boiled with water to expel alcohol, and then sodium acetate was added to precipitate the dyestuff. It was partly purified by dissolving in sulphuric acid and precipitating with sodium acetate, and finally obtained in a pure state by debenzoylating the crystalline benzoyl derivative by boiling its alcoholic solution with sulphuric acid. The

dyestuff could not be crystallised. It dyes chrome-mordanted wool to a red shade which is not brilliant:

0·1055 gave 7·6 c.c. N_2 at 33° and 760 mm. $N = 8·03$.

$C_{23}H_{22}O_3N_2$ requires $N = 7·6$ per cent.

The leuco-compound can be obtained by reducing the dyestuff with zinc dust and acetic acid, but is oxidised again to the dyestuff on coming into contact with air. The *monobenzoyl* derivative of the dyestuff was prepared by the Schotten-Baumann reaction in the ordinary way. It is soluble in all the common solvents. By the spontaneous evaporation of a cold chloroform solution it crystallises in prismatic needles melting at 125°:

0·1665 gave 8·0 c.c. N_2 at 33° and 763·2 mm. $N = 5·42$.

$C_{30}H_{27}O_4N_2$ requires $N = 5·8$ per cent.

$2 : 3 : 7$-*Trihydroxy-9-o-p-dihydroxyphenyl-6-fluorone.*

One gram of $2 : 4$-dihydroxybenzaldehyde and 2 grams of hydroxyquinol were dissolved in 10 c.c. of 50 per cent. alcohol; 1·5 c.c. of sulphuric acid (D 1·84) were then added, and the mixture was heated on the water-bath for fifteen minutes, when the fluorone *sulphate* was precipitated. It was collected and washed with 50 per cent. alcohol:

0·5475 gave 0·1800 $BaSO_4$. $H_2SO_4 = 12·5$.

$(C_{19}H_{14}O_7)_2H_2SO_4$ requires $H_2SO_4 = 12·15$ per cent.

The dyestuff was obtained by boiling the sulphate with water for one and a-half hours. It could not be crystallised. It dissolves in potassium hydroxide solution with a reddish-violet colour, and dyes chrome-mordanted wool in fine, reddish-violet shades. Acetylation resulted in the production of a mixture of derivatives which could not be separated by fractional crystallisation:

0·1200 gave 0·2805 CO_2 and 0·0405 H_2O. $C = 63·75$; $H = 3·75$.

$C_{19}H_{14}O_7$ requires $C = 64·4$; $H = 3·95$ per cent.

$1 : 3 : 8$-*Trihydroxy-9-o-p-dihydroxyphenyl-6-fluorone.*

One gram of $2 : 4$-dihydroxybenzaldehyde and 2 grams of phloroglucinol were dissolved in 10 c.c. of 50 per cent. alcohol, and 1·5 c.c. of sulphuric acid (D 1·84) were then added. After shaking for two minutes, orange-coloured needles of the fluorone *sulphate* began to form. They were collected and washed with 50 per cent. alcohol:

0·5000 gave 0·1515 $BaSO_4$. $H_2SO_4 = 12·4$.

$(C_{19}H_{14}O_7)_2H_2SO_4$ requires $H_2SO_4 = 12·15$ per cent.

The dyestuff was obtained by boiling the sulphate for one and

a half hours with water. It could not be crystallised. It dissolves with an orange colour in potassium hydroxide solution and dyes chrome-mordanted wool in orange shades:

0·1000 gave 0·2350 CO_2 and 0·0330 H_2O.   C=64·09; H=3·66.
$C_{19}H_{14}O_7$ requires C=64·4; H=3·95 per cent.

The experimental work described in this paper has been done entirely by P. C. Ghosh.

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LXX.—*The Absorption Spectra of Substances containing Conjugated and Unconjugated Systems of Triple Bonds.*

By ALEXANDER KILLEN MACBETH and ALFRED WALTER STEWART.

IT has long been known that saturated substances possess an absorptive power much lower than that shown by the corresponding ethylenic derivatives; and further investigations have proved that of two isomeric diethylene derivatives, that which contains a conjugated system of double linkings has a greater absorptive power than the isomeride in which the ethylenic bonds are isolated from each other (Crymble, Stewart, Wright, and Glendinning, T., 1911, **99**, 451; Crymble, Stewart, Wright, and Miss Rea, *ibid.*, 1262). The present investigation was undertaken with the idea of testing whether or not a similar rule could be established in the case of acetylenic derivatives, but the results show that no such generalisation can be looked for in this series. The data, however, are of some interest from other points of view.

It was decided to examine acetylenic compounds belonging to both aliphatic and aromatic series. Some of the latter class had already been investigated by Stobbe (*Ber.*, 1911, **44**, 1289), but no general rule could be deduced from his results, as the phenyl nucleus might be expected to interfere with the influence of the acetylenic linking to some extent.

It will probably render the data clearer if the discussion of each group of compounds be taken separately, final conclusions being reserved until the whole facts have been reviewed.

Series I. Behenolic Acid and Erucic Acid (Fig. 1, *A*).—Here

the ethylenic derivative is much more absorbent than the acetylenic analogue. In this case, the effect of the double and triple linkings may be taken as being unaffected by the presence of the carboxyl radicle, from which they are separated by eleven methylene groups.

Series II. Stearolic Acid, Elaidic Acid, and Stearic Acid (Fig. 1, *B*).—In this case, the acetylenic derivative is the most strongly absorbent, the ethylenic next, and the saturated substance least of all. The only factor that might account for this marked absorptive power of the acetylenic substance is to be found in the fact that the carbonyl radicle of the carboxyl group is

FIG. 1.

Oscillation frequencies.

——— Behenolic acid.	——— Stearolic acid.	········· Acetylenedicarboxylic acid.
—·—·— Erucic acid.	—··—··— Elaidic acid.	·—··— Fumaric acid.
	- - - - - Stearic acid.	—·····— Maleic acid.
		- - - - Succinic acid.

A.   *B.*   *C.*
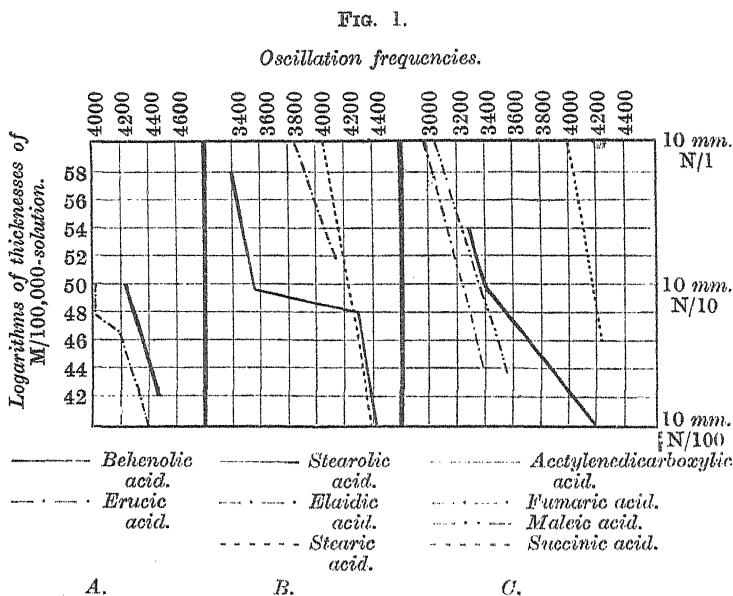
situated at the ninth carbon atom from both the triple and double linkings, which would imply, under the usual assumptions as to the arrangements of carbon chains in space, that the unsaturated centres were spatially conjugated with two turns of the spiral between them. It is sufficient to indicate this and leave the matter without further elaboration.

Series III. Acetylenedicarboxylic Acid, Fumaric Acid, Maleic Acid, and Succinic Acid (Fig. 1, *C*).—As can be seen from the graph, the two ethylenic isomerides are more absorptive than the acetylenic compound—fumaric acid being markedly so—and succinic acid is least absorptive of all.

Series IV. Di-iodoacetylene, Di-iodoethylene, and Ethylene Iodide (Fig. 2).—This case presents a fresh problem. The saturated compound, ethylene iodide, possesses a distinct absorption band having its head at a frequency of 3900, and this band is directly attributable to the presence of the two iodine atoms

FIG. 2.

Oscillation frequencies.

Logarithms of thicknesses of N/100,000-solution.

———— *Di-iodoacetylene.*
— · —— · — *Di-iodoethylene.*
- - - - - - - *Ethylene iodide.*
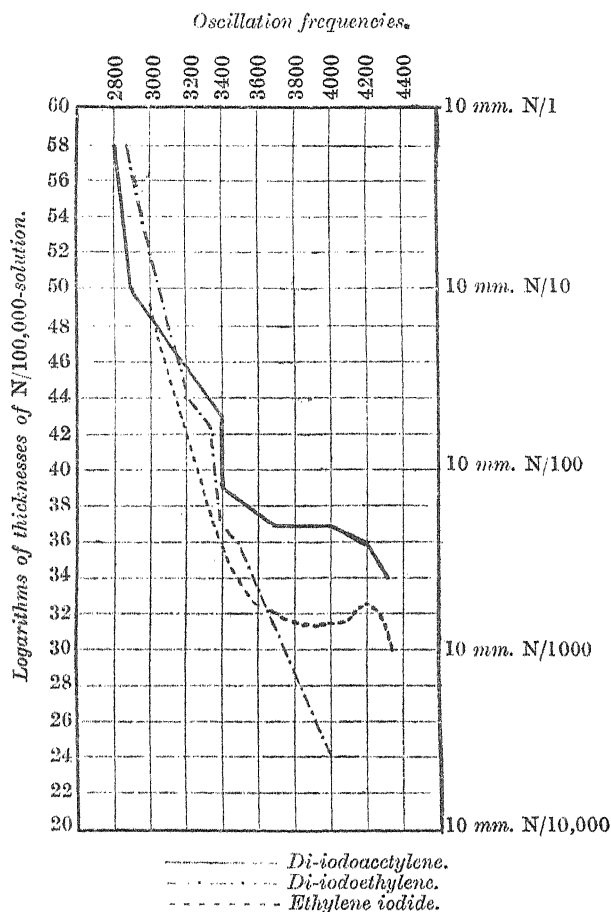
in the molecule. Now the introduction of fresh unsaturated centres in the molecule might have either of two effects, since there may be an enhancement of the band due to stimulation of the process which produces it, or, conversely, a cancellation of affinity leading to a decrease in absorptive power. An inspection of the

curves shows that the second process is in operation to some extent, for the acetylenic compound is much less absorptive than the saturated substance. The absorption of di-iodoacetylene is limited to a frequency of 4200 at a logarithmic thickness of 36, whereas the corresponding ethylenic compound continues to absorb to the same extent in a logarithmic thickness of 32. Further, the absorptive power of the acetylenic compound is, except for a portion in the visible region of the curve, actually less than that of the aliphatic analogue, from which it must be deduced that the introduction of the triple bond into the molecule has considerably influenced the absorptive power of the iodine atoms. On the other hand, by the same reasoning, the ethylenic linking has an effect opposite to that of the triple bond, whether this be attributable to a stimulation of the iodine vibration by the affinity of the residual affinity of the carbon atoms or merely to the increase in absorptive power usually noted when passing from the paraffin to the olefine derivatives.

Series V. Dimethyldiacetylene, Hexatriene, Benzene †* (Fig. 3). —This case is one of the most interesting of all those which have yet been examined. A comparison of the structural formulæ of the three compounds must first be made :

C_6H_6 Dimethyldiacetylene $CH_3—C{\equiv}C—C{\equiv}C—CH_3$

C_6H_8 Hexatriene $CH_2{=}CH—CH{=}CH—CH{=}CH_2$

C_6H_6 Benzene $CH{=}CH—CH{=}CH—CH$
                            CH
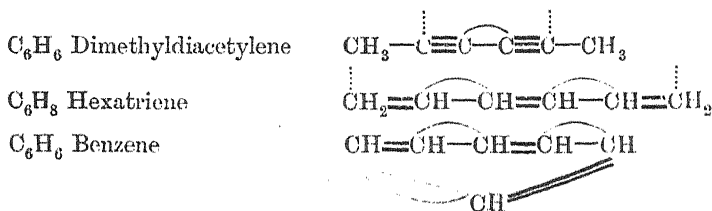
It will be noticed that dimethyldiacetylene and benzene are isomeric, whilst hexatriene contains an extra pair of hydrogen atoms, and from this it might be expected that the first two substances would show greater absorptive power than hexatriene. An examination of the curves in Fig. 3 shows that this deduction is unwarranted; contrary to the usual rule, the more saturated substance is the most strongly absorbent, except just at the very top of the curve.

In order to explain this apparent anomaly, it is necessary to bear in mind what has already been said with respect to the influence of conjugation. Take, first, the case of benzene and hexatriene. In the benzene nucleus there are three double linkings, but these

* This curve is taken from Baly and Tuck, T., 1908, **93**, 1909.

† This curve is taken from Baly and Collie, *ibid.*, 1905, **87**, 1332, the banded region being indicated by shading.

three linkings saturate each other and form a completely linked
system with no free partial valencies. In the case of hexatriene,
on the other hand, although in its molecule there are also three
conjugated double linkings, these double linkings do not com-
pletely saturate each other, for there is a considerable amount of

FIG. 3.

Oscillation frequencies.

Dimethyldiacetylene.
Hexatriene.
Benzene with banded region shown by shading.
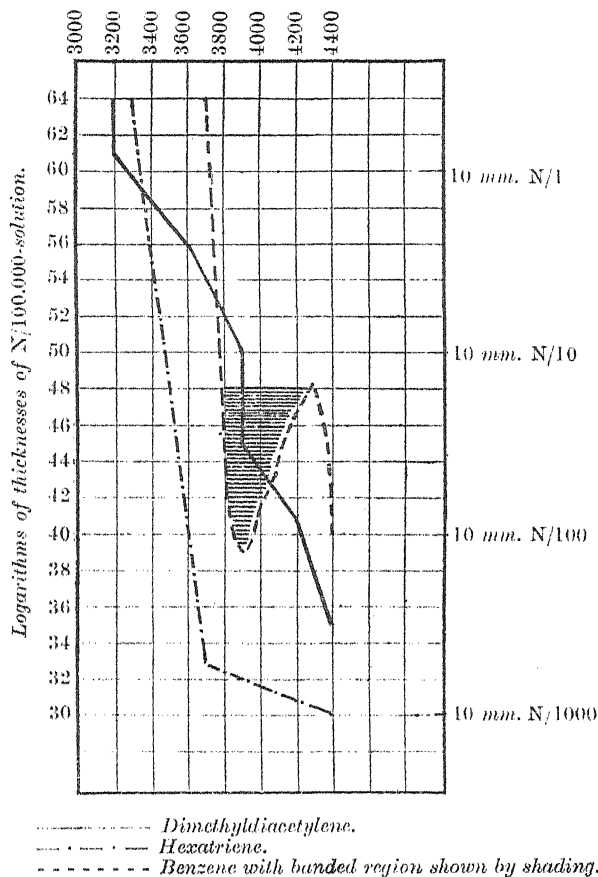
residual affinity left untouched at each end of the chain. From
this it may be deduced that the presence of free affinity (or partial
valencies) tends to increase absorptive power, which is borne out
by the well-known fact that the introduction of any unsaturated
centre into a molecule enhances the power of absorption.

A further step in advance is found when the case of dimethyl-diacetylene is considered in conjunction with the foregoing. Dimethyldiacetylene contains two conjugated double linkings, and it is reasonable to assume that to some extent these will behave like two conjugated double bonds, saturating each other to a certain degree, but leaving a considerable amount of residual affinity at either end of the chain. In the case of the acetylene derivative, however, there is not the same long chain of conjugation which is present in the case of the hexatriene molecule. The whole residual affinity of the acetylenic compound is concentrated in two centres in close proximity to one another. Thus in hexatriene we find two active centres far removed from each other; dimethyldiacetylene contains two centres of residual affinity sufficiently near one another to interfere with each other, and hence reduce the amount of free affinity present, whilst benzene contains no independent centres of partial valency under normal conditions. Further, the absorptive powers of the three compounds stand in this order also.

It may reasonably be suggested that absorptive power is greatest when a molecule contains more than one centre of residual affinity and when such centres are so situated as to be incapable of mutual interference. Under such an assumption, it would be expected that of two stereoisomerides, for example, the fumaroid form would exhibit most absorptive power, a conclusion which is borne out by facts. For instance, an examination of Fig. 1, C, shows that maleic acid is much less absorptive than fumaric acid. An examination of their spatial formulæ indicates that in the case of fumaric acid the two accumulations of residual affinity at the ends of the chain are sufficiently far removed from one another to preclude mutual interference, whereas in the case of maleic acid they are near together.

Fumaric acid.   Maleic acid.
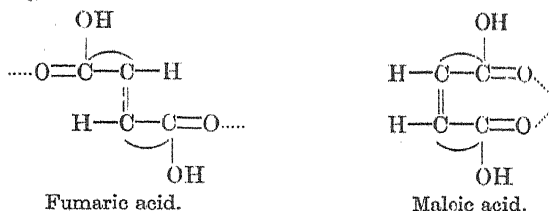
Further support of this view will be found in the facts described in Series IX.

Series VI. Phenylacetylene, Styrene (Phenylethylene), and Ethylbenzene (Fig. 4).—In this case the ethylenic derivative exhibits the greatest power of absorption; the acetylenic compound stands next in order, and the ethane derivative has least absorptive

power. These data hold good whether the absorptive power be
judged by the wave-length absorbed by a given thickness of solu-
tion or by the dilution to which absorption persists. As regards
the manner of absorption, in the case of ethylbenzene the region
of banded absorption in benzene itself is occupied by a broader

Fig. 4.

Oscillation frequencies.
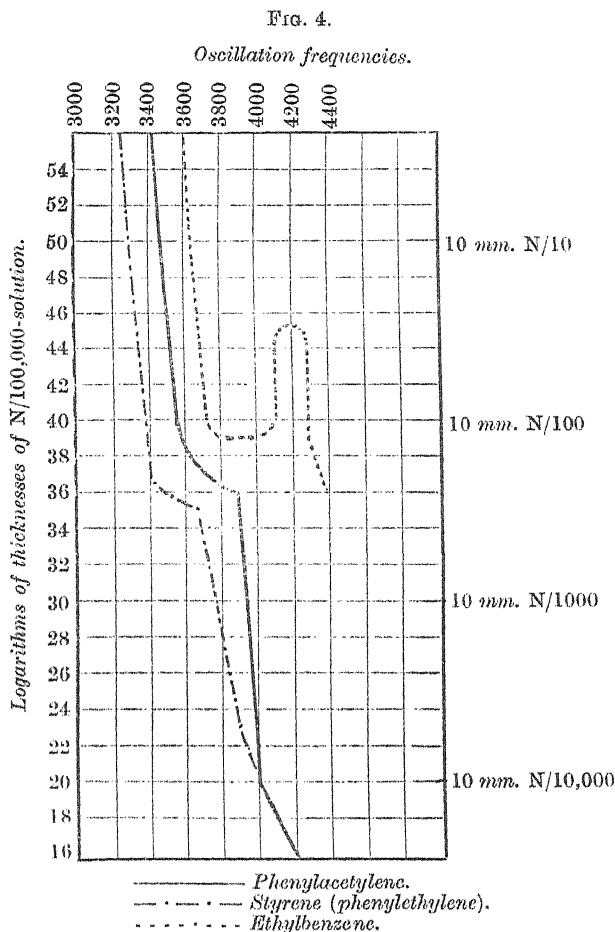
single band, and it appears that the introduction of the ethyl
radicle into the benzene nucleus has no marked effect on the
character of the absorptive power. There is no increase in the
persistence of the band. With styrene (phenylethylene) and
phenylacetylene, on the other hand, there is an increase in general
absorptive power as compared with benzene itself, which increase

can be attributed only to the effect of introducing the new unsaturated centre into the molecule.

Series VII. Tolane, Stilbene, and s-Diphenylethane (Fig. 5).—The introduction of a second phenyl nucleus into the molecules mentioned in the last section leads to somewhat peculiar results.

FIG. 5.

Oscillation frequencies.

Tolane.
Stilbene.
s-*Diphenylethane.*
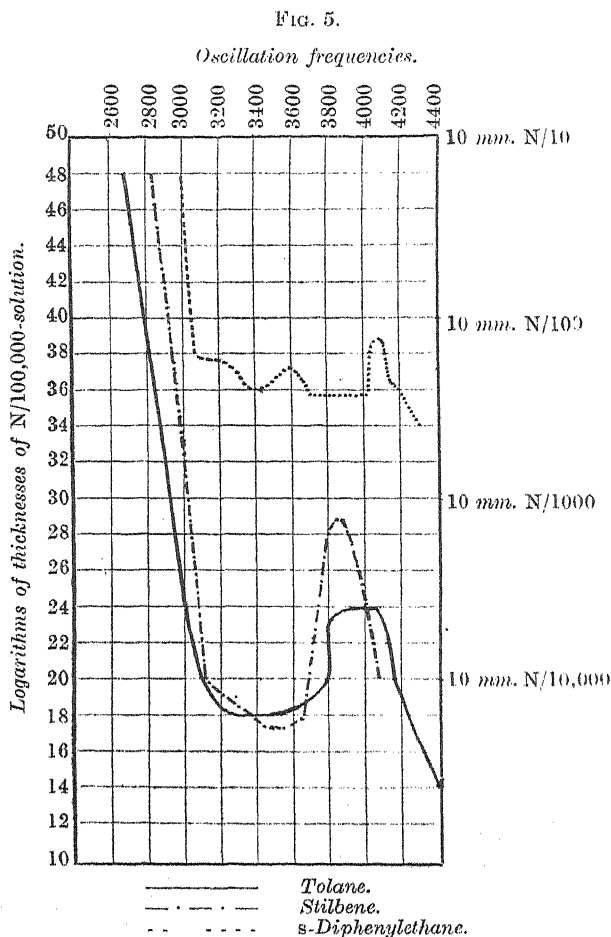
In the case of s-diphenylethane, the graph shows that banded absorption still persists, but that it is completely modified in character. In the first place, the absorptive power is increased, as the band appears at a greater dilution in the s-diphenylethane spectrum than was found to be the case in phenylethylene. Further, instead of a single narrow band, s-diphenylethane shows

a band extending roughly from 3100 to 4100, although it is much shallower than the band of ethylbenzene and shows a tendency to split up into two smaller bands.   One of these narrow bands extends from 3600 to 4100, and thus corresponds roughly with the characteristic band of ethylbenzene; the other band has its head at 3400, and does not occur at all in the spectrum of ethylbenzene. Its appearance must therefore be attributed to the introduction of the second phenyl radicle into the molecule.

Turning to the ethylene derivative, stilbene, it will be observed that it possesses an absorptive power markedly greater than that exhibited by the ethane analogue.   Further, there is no sign whatever of the band characteristic of ethylbenzene; in fact, at this point of the spectrum there is especially good transmission.   On the other hand, the band at 3400 traceable in the spectrum of s-diphenylethane is here broadened and deepened to a very remarkable extent.   It seems probable that the two bands arise from a common cause, but that in the case of stilbene the absorptive power is reinforced by the presence of the long chain of conjugated linkings, seven in number, which exists in the molecule of the ethylenic compound.

In their banded absorption, the ethylenic and acetylenic analogues are approximately similar, but it will be seen from the graph that the band in stilbene extends over a much greater range of dilution than that exhibited by tolane.   This fact reinforces the idea that the band of stilbene is in some way influenced by the conjugated chain, for in the case of tolane the conjugation is imperfect as compared with that of stilbene.   In stilbene, the conjugated chain is made up completely of double and single bonds, whereas in tolane it contains single bonds alternating with double and triple linkings.   Thus, instead of having the whole of the free affinity of the molecule concentrated at two points far removed from each other, as in stilbene, the tolane molecule has two main concentrations plus some excesses of affinity at the ends of the triple bonds.
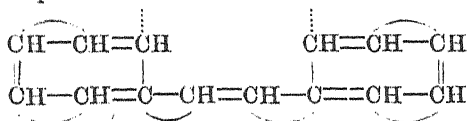
Stilbene.
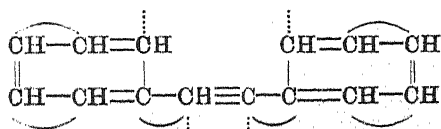
Tolane.

In this way, the contentions put forward in connexion with Series
V. receive further support.

*Series VIII. Phenylpropiolic Acid, Cinnamic Acid, and
β-Phenylpropionic Acid* (Fig. 6).---In this series, the saturated
member of the group shows very much less absorptive power than

Fig. 6.

Oscillation frequencies.

Phenylpropiolic acid.
Cinnamic acid.
β-Phenylpropionic acid.
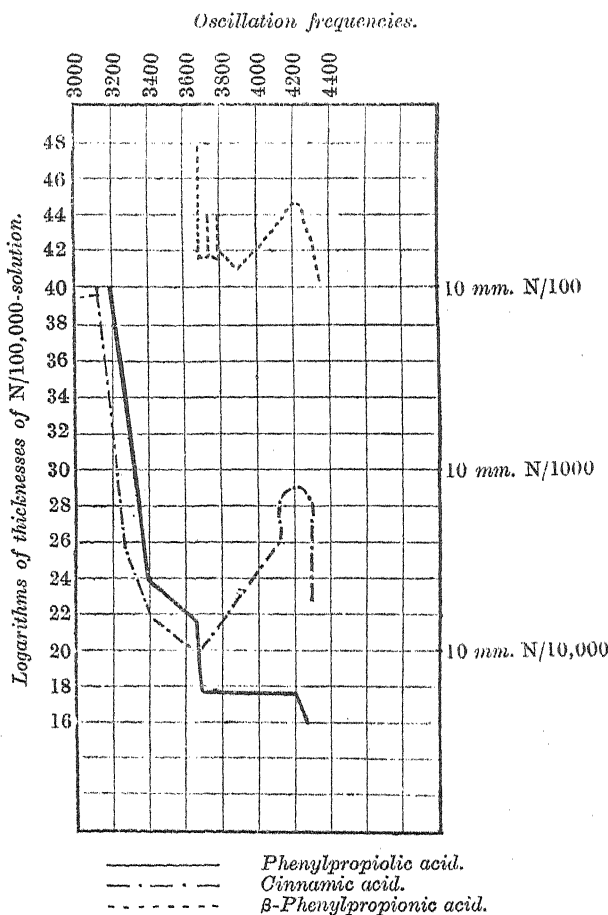
either of the other two. Traces of a modified benzenoid vibration
are to be found in the one broad and two narrow bands which
extend from 3700 to 4200; the dilution at which these bands occur
is approximately the same as that at which the benzene bands
make their appearance.

Cinnamic acid and phenylpropiolic acid show a somewhat similar power of absorption through a certain range of the graph, although cinnamic acid absorbs slightly longer wave-lengths, whilst phenylpropiolic acid shows an absorptive-power at a dilution much higher than that at which cinnamic acid ceases to absorb markedly. Further, cinnamic acid shows a well-defined band of considerable

FIG. 7.

Oscillation frequencies.

Ethyl phenylpropiolate.
Cinnamylideneacetic acid.
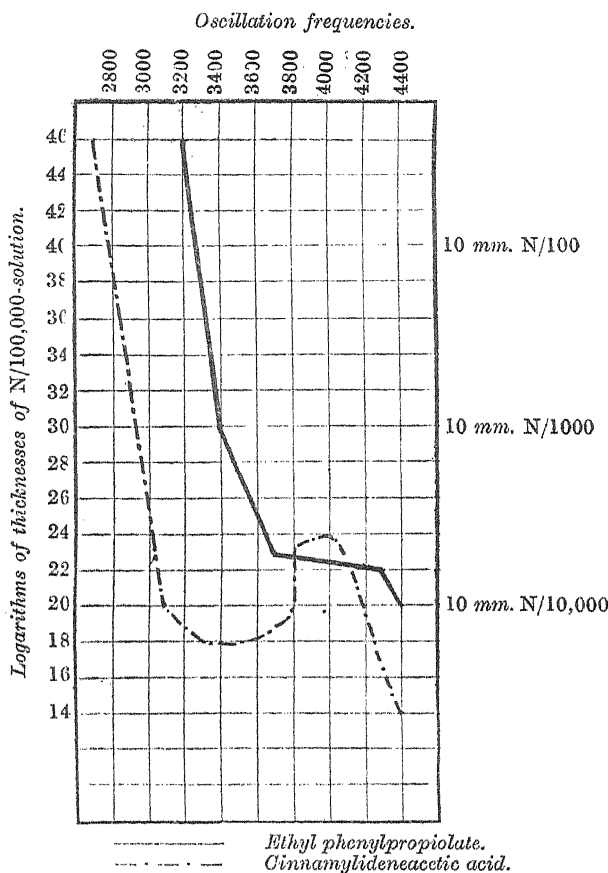
persistence in the region 3300—4200, whereas phenylpropiolic acid exhibits a "step-out" at a higher dilution. Testing the absorptive power by the length of the light-waves absorbed, the order is: ethylenic, acetylenic, and saturated, but as regards the power of absorbing at greatest dilution, they stand in the order of saturation, the acetylenic derivative having most absorptive capacity.

Series IX.   Ethyl Phenylpropiolate and Cinnamylideneacetic Acid (Fig. 7).—This case furnishes another example of the phenomenon which was discussed in Series V. The two compounds, ester and acid, are isomerides, so that, as far as additive factors go, they should exhibit the same absorptive power. An examination of their structural formulæ shows that in the one case there is a long chain of conjugated double bonds in the molecule, so that the residual affinity is concentrated at two distant points, whereas in the other case the affinity centres are nearer together and are more likely to disturb one another :

CH—CH=CH·····   OH
‖ | |
CH—CH=C—CH=CH—CH=CH—C=O·····

Cinnamylideneacetic acid.

CH—CH=CH·····   O·C$_2$H$_5$
‖ |
CH—CH=C—C≡C—C=O

Ethyl phenylpropiolate.

From what has already been said on this matter, it may be deduced that cinnamylideneacetic acid will show the greatest absorption, whilst the absorptive power of ethyl phenylpropiolate will be considerably less. An examination of the graphs shows that this prophecy is justified. The absorptive power of the ester is less than that of its isomeride, both from the point of view of the wave-length absorbed by a fixed concentration and also from the point of view of the dilution at which the substance continues to show absorption.

Thus, although the examination of acetylenic derivatives has not brought to light any close parallel between them and the ethylenic analogues so far as light-absorbing power is concerned, it has elicited new facts with regard to the influence exerted by the distribution of residual affinity in the molecule on the absorptive power of the substance. At the present time our knowledge of the subject in its broadest outlines may be summarised as follows: The introduction of a centre of residual affinity into a saturated molecule increases that molecule's power of absorbing light. The introduction of a second centre of residual affinity into the molecule normally increases the absorptive power, although in some cases (such as the iodine compounds) it may act in a converse manner. If the two centres of residual affinity are placed so far apart in the molecule, either spatially or structurally, that

they fail to exert any mutual influence on one another, then the absorptive power of the molecule is greater than is found to be the case when the same amount of residual affinity is concentrated in two adjacent points of the molecule.

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　　　　　　　　THE UNIVERSITY OF GLASGOW.

LXXI.—The Uniform Movement of Flame in Mixtures of Acetylene and Air.

By WILLIAM ARTHUR HAWARD and SOSALE GARALAPURY SASTRY.

IN continuation of the revision of previous work on the propagation of flame that is being carried out at the Home Office Experimental Station under the direction of Dr. R. V. Wheeler, we have determined the speeds of the "uniform movement" in mixtures of acetylene and air.

It may be recalled that the "uniform movement" occurs when an inflammable mixture of gases is ignited at the open end of a horizontal tube closed at the other end, and is usually regarded as the normal speed of propagation of flame from layer to layer of the mixture by conduction of heat (Mallard and Le Chatelier, *Ann. des Mines*, 1883, [viii], **4**, 374).

Previous determinations of the speed of the uniform movement in mixtures of acetylene and air have been made by Le Chatelier (*Compt. rend.*, 1895, **121**, 1144), who used a glass tube 4 cm. in diameter. The speeds recorded were:

Acetylene in mixture. Per cent.	Speed of uniform movement. Cm. per second.
2·9	10
8·0	500
9·0 and 10·0	600
22·0	40
64·0	5

In a later publication, namely, "Le Carbone" (Paris, 1908), Le Chatelier gives intermediate values:

Acetylene in mixture. Per cent.	Speed of uniform movement. Cm. per second.
5·0	200
7·0	400
15·0	300
40·0	22
60·0	7

but it is not clear whether these are actual determinations or numbers interpolated on a curve constructed from the six results recorded in the *Comptes rendus*.

Le Chatelier thus describes the curve he obtained (*loc. cit.*, p. 280):

"La courbe . . . présente une forme toute spéciale; elle se compose de trois droites: une droite montante et une descendante se coupant pour la vitesse maxima vers 10 p. 100 d'acétylène, puis ensuite une droite tres peu inclinée coupant la second à la teneur de 20 p. 100 et se prolongeant jusqu'à la limite d'inflammabilité supérieure. Ce troisième segment de la courbe correspond à la combustion avec flamme fuligineuse et dépôt de charbon. Au-dessous de 20 p. 100 il ne se forme par la combustion que des produits gazeux, acide carbonique, oxyde de carbone et hydrogène."

Our own experiments were made in a glass tube 12 mm. in diameter, and are not therefore directly comparable with Le Chatelier's so far as the absolute measurements of speeds are concerned. It is permissible, however, to compare the shapes and characters of the two curves. We can confirm the statement that mixtures containing more than about 20 per cent. of acetylene deposit soot owing to decomposition of excess of acetylene, and that the speed of propagation of flame in such mixtures is slow; but we cannot agree that the curve can be represented by straight lines. As with mixtures of other inflammable gases and air, there is a gradual flattening of the curve towards the limits, and the maximum speed is obtained over a range of mixtures containing between 8 and 10 per cent. of acetylene, so that the crest of the curve also is flattened.

Our results are shown graphically in the diagram. The speed of the flame in mixtures containing more than 20 per cent. of acetylene decreases gradually as the percentage of acetylene is increased. The mixture of acetylene and air for complete combustion contains 7·75 per cent. of acetylene; the fact that the fastest speed of flame is found in mixtures containing rather more than this can be explained on the assumption that the thermal conductivity of acetylene is higher than that of air (compare Haward and Otagawa, T., 1916, **109**, 83).

EXPERIMENTAL.

The method of experiment and the electrical means of measuring the speeds of the flames were the same as employed by Wheeler (T., 1914, **105**, 2606).

The acetylene was obtained compressed in cylinders, without acetone as solvent, and was of a high degree of purity (98 to 99

per cent. C_2H_2). The mixtures were made over brine in metal gas-holders of 70 litres capacity, and were analysed before use; the explosion tube was filled with the required mixture by displacement of air, six times the volume of the tube being used. The initial temperature of the mixtures was that of the room (15° to 20°), and they were saturated with water-vapour at that temperature.

Ignition was by means of a lighted taper, which was drawn rapidly past the open end of the tube. The speeds were measured
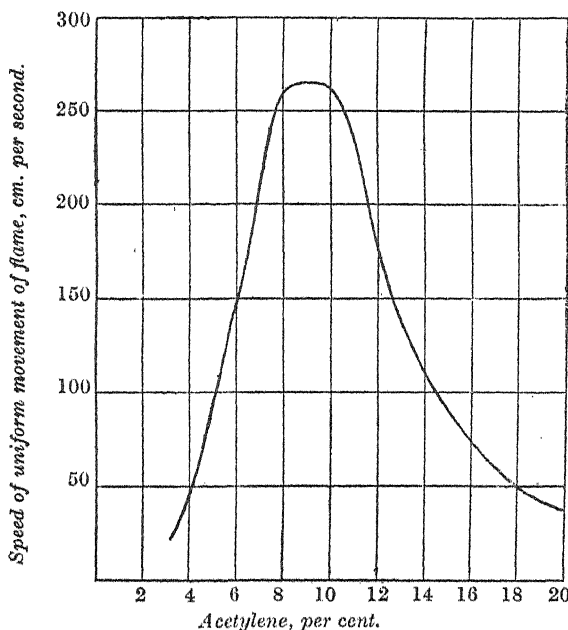
between two points 40 cm. apart, the first point being 10 cm. from the open end of the tube.

In addition to the experiments recorded in the diagram, for which a tube 12 mm. in internal diameter was used, the speeds in tubes of 9 mm. and 25 mm. diameter were also determined. The speeds in the 9 mm. tube were rather slower than those obtained in the 12 mm. tube, but the shape of the curve was the same. With the larger tube, 25 mm., the duration of the uniform movement was too short to admit of accurate measurement by the means employed.

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LXXII.—*Methylation by Means of Formaldehyde. Part I. The Mechanism of the Interaction of Formaldehyde and Ammonium Chloride; The Preparation of Methylamine and of Dimethylamine.*

By EMIL ALPHONSE WERNER.

THE preparation of methylamine from formaldehyde and ammonium chloride is perhaps not so well known as it certainly deserves to be. Having occasion to make use of this reaction from time to time during the last few years, the author has studied this interesting and important change, the mechanism of which, it must be admitted, has up to the present remained decidedly obscure.

Several new facts have been brought to light which have greatly helped to disclose what is now believed to be the true mechanism of the progressive changes involved in this rather complex reaction.

The interaction of formaldehyde and ammonium chloride was first examined by Plöchl (*Ber.*, 1888, **21**, 2117), who, from a rather superficial study of the change, observed the formation of tri-methylamine and the evolution of carbon dioxide. No attempt was made to give an explanation of the reaction whereby the amine was produced.

Some years later Brochet and Cambier (*Compt. rend.*, 1895, **120**, 449, 557; *Bull. Soc. chim.*, 1895, [iii], **13**, 392) reinvestigated this reaction, and showed what were the best conditions for the economic preparation of methylamine hydrochloride by its means.

The explanation which they have given, of what they considered to be the main reaction, is far from satisfactory, and they have been decidedly at fault in their observations concerning certain experimental facts connected with the reaction.

As a result of their investigations, they have drawn the conclusion that whilst methylamine is almost the sole product when ammonium chloride is used in excess, trimethylamine is the main product when formaldehyde is in excess.

The latter conclusion has not been confirmed.

These investigators have evidently mistaken impure dimethylamine hydrochloride for the salt of the tertiary base, only a small quantity of which has been detected when formaldehyde was used in excess, and even then only when a relatively high temperature was attained.

As regards their explanation of the reaction, Brochet and Cambier have drawn the conclusion that "formaldehyde condenses

with ammonium chloride in a very complex manner"; it has been assumed that trimethylenetriamine hydrochloride, $(CH_2:NH,HCl)_3$, is at once formed, as a result, probably, of the polymerisation of methyleneimine, $CH_2:NH$, produced in the first instance; the polymeride then condenses further with formaldehyde, whether the latter is present in excess or not, to give methylamine hydrochloride, according to the equation

$$2(CH_2:NH,HCl)_3 + 3CH_2O + 3H_2O = 6CH_3 \cdot NH_2,HCl + 3CO_2.$$
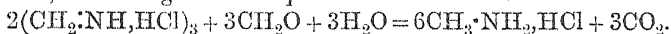
When the aldehyde is present in large excess, they state, "on arrive finalement au chlorhydrate du trimethylamine par une serie de réactions identiques," that is, the compound,

$$(CH_2:N \cdot CH_3,HCl)_3,$$
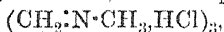
is formed, which in its turn condenses with formaldehyde to form carbon dioxide, methylamine, and trimethylamine.

It must be admitted that the above equation still leaves the question of the origin of methylamine rather obscure, let alone the case of trimethylamine.

More recently, Knudsen (*Ber.*, 1914, **47**, 2694) has re-examined this reaction, and whilst he has forestalled the author in showing that dimethylamine was produced, he has not added any useful information towards the elucidation of the mechanism by which the amines take origin. Thus it has been assumed that dimethylamine and trimethylamine are produced from the decomposition of a complex, not to say doubtful, dimethylpentamethylenetetramine formed in the first instance as a result of the union of methylamine with excess of formaldehyde.

In both cases, then, obscure condensation reactions have been regarded as explaining the formation of all three amines. This, it will be shown, is quite unnecessary in order to explain the different changes, and, moreover, such a view is in contradiction to the observed facts.

Mechanism of the Formation of Methylamine and of Dimethylamine.

When a solution of ammonium chloride and formaldehyde (commercial formalin), in the proportions recommended by Brochet and Cambier, was gradually heated, a volatile liquid began to distil at 50°; after heating at 104° until distillation had practically ceased, the amount of distillate obtained was equal to 22 per cent. of the weight of the formaldehyde solution taken. This distillate has been considered by Brochet and Cambier to consist of methylal and water only; thus they state that the product may contain from 60—79 per cent. of the former.

Whilst methylal formed a considerable portion of the distillate,

the chief constituent was methyl formate, an important fact which Brochet and Cambier have completely overlooked. The composition of the distillate was fairly constant, whether ammonium chloride or formaldehyde was present in an excess at the outset.

When methylamine hydrochloride and formaldehyde were heated in solution, 90° was reached before distillation was observed; the distillate contained methylal and methyl formate in nearly equal proportions; on the other hand, from dimethyl-ammonium chloride and formaldehyde, after heating under similar conditions, a distillate was obtained which contained practically no methyl formate.

The following results represent the average composition of the distillates in the three respective cases:

	(I.)	(II.)	(III.)
		NH_3MeCl+	NH_2Me_2Cl+
Percentage composition	$NH_4Cl+CH_2O.$	$CH_2O.$	$CH_2O.$
of distillate.	$t=104°.$	$t=104°.$	$t=110°.$
Methyl formate	$=39.0$	13.10	0.13
Methylal....................	$=34.6$	13.32	8.70
Free formic acid	$= 1.6$	3.64	2.80
Water......................	$=24.8$	69.94	88.37
	CO_2 freely	CO_2 freely	a trace of
	evolved.	evolved.	CO_2 evolved.

Whilst the formation of methylal is a normal result of a reaction between formaldehyde and methyl alcohol (present in commercial formalin) promoted by hydrochloric acid set free during the process, the production of methyl formate (and carbon dioxide) in considerable quantity furnishes an important clue to the mechanism of the reaction. The oxidation of formaldehyde to formic acid, and of the latter to carbon dioxide, must, in the present circumstances, be provoked by the presence of another substance having an equal tendency to undergo reduction. Through the decomposition of water the desired result is attained, a simultaneous oxidation and reduction is brought about, and as a result of the latter, methylamine and dimethylamine are produced in accordance with the following scheme.

The first phase of the change gives rise to methyleneimine, thus:

$$(1) \quad H\cdot COH + NH_3(HCl)* \longrightarrow H\cdot CH{<}^{OH}_{NH_2} \longrightarrow$$

$$CH_2\text{:}NH(HCl) + H_2O$$
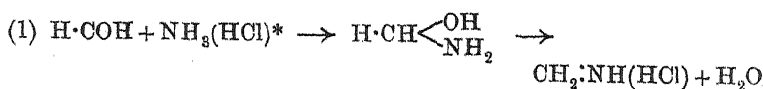
It is the great tendency of formaldehyde to react with ammonia that no doubt determines a rapid dissociation of the haloid salt;

* When ammonium chloride and formaldehyde are mixed in solution, the liquid quickly becomes strongly acid from liberation of hydrogen chloride; the brackets are used here to indicate the dissociated salt.

the feeble base $CH_2:NH$ remains largely dissociated, since titration, using phenolphthalein as indicator, shows all the hydrochloric acid to be in the free state. Its presence, however, prevents polymerisation of the base, and equilibrium (that is, neutralisation) is rapidly established by reduction and oxidation, thus:

(2) $CH_2:NH(HCl) + H_2O + H \cdot COH = CH_3 \cdot NH_2,HCl + H \cdot CO_2H,$
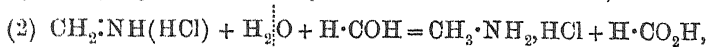
and whilst part of the formic acid is neutralised by esterification, the larger portion is oxidised to carbon dioxide and water.

As the temperature rises, the main reaction (2) is soon accompanied by a change similar to (1), in which methylammonium chloride takes part, whereby dimethylammonium chloride is ultimately formed, thus:

(3) $CH_2O + NH_2 \cdot CH_3(HCl) = CH_2:N \cdot CH_3(HCl) + H_2O.$

(4) $CH_2:N \cdot CH_3(HCl) + H_2O + H \cdot COH = (CH_3)_2NH,HCl + H \cdot CO_2H.$
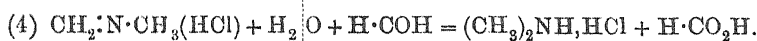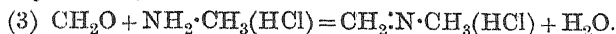
The next and final phase in the change is the result of a reaction between formaldehyde and dimethylammonium chloride, thus:

(5) $CH_2O + 2NH(CH_3)_2(HCl) = CH_2 \begin{subarray}{l} N(CH_3)_2,HCl \\ N(CH_3)_2,HCl \end{subarray} + H_2O.$
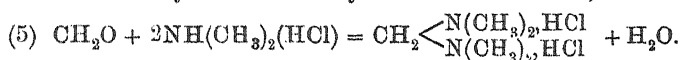
and since a stable saturated base is produced it will show no tendency to suffer reduction, and consequently there will be no oxidation of formaldehyde during this phase, as shown by the results obtained under III.

In accordance with this scheme, therefore, trimethylamine cannot be directly formed during the progress of the changes which give rise to the primary and secondary bases, and this explains why it has not been detected in the reaction product when the temperature was not allowed to rise above, say, 110°.

If, on the other hand, the temperature be carried too high, as was the case in Knudsen's experiments (*loc. cit.*). or the heating be unduly prolonged, a condition which can scarcely be avoided in dealing with the final mother liquors, after the separation of the bulk of the chlorides of methylammonium and of dimethylammonium, then some trimethylamine is undoubtedly produced. The evidence goes to show that the tertiary base, very probably, arises from the decomposition of the above methylene base, thus:

(6) $CH_2 \begin{subarray}{l} N(CH_3)_2 \\ N(CH_3)_2 \end{subarray},2HCl = N(CH_3)_3,HCl + CH_2:N \cdot CH_3(HCl).$
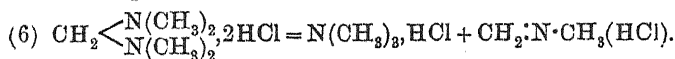
The unsaturated base, in the absence of excess of formaldehyde, is polymerised to the compound $(CH_2:N \cdot CH_3)_3$,* the presence of which

* This base has been prepared by Henry (*Bull. Acad. roy. Belg.,* 1893, [iii], **26**, 200), and later by Brochet and Cambier (*loc. cit.*), who determined its molecular weight.

can be shown by the formation of a copious precipitate on addition of picric acid. The picrate (m. p. 127°, Duden and Scharff, *Ber.*, 1895, **28**, 936) cannot be crystallised from water on account of the ease with which it dissociates.

Since the changes represented by equations (2) and (4) overlap during the progress of the reaction, the production of dimethylammonium chloride in moderate quantity cannot be avoided. Its separation from a considerable amount of methylammonium chloride is, however, a very simple matter, as described later on.

By adopting such conditions as were indicated by the above scheme, a very large yield of dimethylammonium chloride has been obtained with the use of much less formaldehyde than was found necessary by Knudsen (*loc. cit.*). The absence of condensation products in the early stages of the reaction, that is, both before and after large quantities of methylammonium and dimethylammonium chlorides have been produced, has been proved by the fact that no precipitation was produced on the addition of picric acid. This reagent forms sparingly soluble compounds with all the condensation products, or polymerides which have hitherto been supposed to play a part in the formation of the primary and secondary bases produced in this interesting and important reaction.

Preliminary experiments have proved the wide scope of the use of formaldehyde for methylating amino-compounds of various types, on the lines of the scheme just recorded. These, it is to be hoped, will be described in the near future.

EXPERIMENTAL.

The Preparation of Methylammonium Chloride.

The proportions of ammonium chloride and formaldehyde (40 per cent. formalin) * recommended by Brochet and Cambier (*loc. cit.*), namely, one part by weight of the former, and two parts by weight of the latter, were found after several trials to give the best results. Since about 35 per cent. of ammonium chloride has always been recovered unchanged, the molecular ratios $NH_4Cl : 2CH_2O$ required by theory are very closely represented by the above proportions.

Expt. I.—Two hundred and fifty grams of ammonium chloride and 500 grams of formaldehyde solution were gradually heated in a distillation flask, which carried a thermometer with the bulb well below the surface of the liquid. The temperature was slowly raised to 104°, and was not allowed to rise above this point, at which it

* Analyses of seven different samples of commercial formalin gave as a mean result 35 per cent. of formaldehyde, and in no case was a sample found to contain 40 per cent. The highest value was 37·4 per cent., the lowest 33·2 per cent.

was maintained until no more volatile liquid distilled; this required about four and a-half hours. The distillate weighed 110 grams. The product was allowed to cool, and after filtration from 62 grams of ammonium chloride which had separated, was concentrated by evaporation at 100° to about one-half of the original volume. After removal of 19 grams of ammonium chloride,* the liquid was again concentrated by evaporation until a crystalline scum had formed on the surface of the hot solution.

After cooling, 96 grams of methylammonium chloride (Found, Cl = 52·46. Calc., Cl = 52·59 per cent.) were separated; after further concentration a second crop (18 grams, Cl = 52·39 per cent.) was obtained. The filtrate was now concentrated as far as possible at 100° and was left for twenty-four hours in a vacuum over sodium hydroxide, after which the semi-solid residue was digested with chloroform, when 20 grams of methylammonium chloride (Cl = 52·63 per cent.) which had been washed with chloroform to remove dimethylammonium chloride, were obtained. The total yield was 128 grams.

From the chloroform solution, after removal of much of the solvent by distillation, 27·5 grams of dimethylammonium chloride were obtained (Found, Cl = 44·38. Calc., Cl = 43·5 per cent.).

A viscous residue (76 grams) which did not crystallise after remaining for a week in a vacuum over sulphuric acid, was finally obtained; it contained Cl = 40·37 per cent. It was distilled, after the addition of an excess of a 40 per cent. solution of sodium hydroxide, and the alkaline vapours evolved were absorbed in an alcoholic solution of hydrochloric acid, when a small quantity of methylammonium chloride and a relatively large quantity of dimethylammonium chloride were obtained, but no trimethylammonium chloride could be detected. Formaldehyde was also regenerated by the action of sodium hydroxide on the viscous material, which no doubt contained much tetramethylmethylenediamine hydrochloride, $CH_2(NMe_2)_2,2HCl$, which requires Cl = 40·57 per cent.

Examination of Volatile Liquid Distillate.—This had D^{15} 0·927. Five c.c. after digestion with 50 c.c. of N-sodium hydroxide required 18·15 c.c. of N-sulphuric acid for neutralisation.

Five c.c., after removal of methyl formate and methylal by heat at 70°, left an acid liquid which required 1·65 c.c. of N-sodium hydroxide for neutralisation. Hence $H\cdot CO_2Me = 39·09$; $CH_2O_2 = 1·62$ per cent. The proportion of methylal was determined by difference after removal of water by anhydrous calcium chloride. The

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* Ammonium chloride is very sparingly soluble in a concentrated solution of methylammonium chloride, and consequently its separation from the latter salt is very sharp.

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separation of methyl formate from methylal by fractional distilla-
tion was found to be an extremely tedious process, and was aban-
doned as useless from an economic point of view. The value of the
distillate is of importance, since all the formic acid can be easily
recovered as sodium formate, after shaking with a solution of sodium
hydroxide in the cold, and thus separated from methylal.

The following results illustrate the value of the whole process
from an economic point of view. From an experiment with 4000
grams of formalin and 2000 grams of ammonium chloride, and
without working up the final viscous residue, there were obtained
1037 grams of pure methylammonium chloride, 218 grams of nearly
pure dimethylammonium chloride, 408 grams of anhydrous sodium
formate, and 264 grams of pure methylal (b. p. 42—43°), whilst
698 grams of ammonium chloride were recovered. The yield of
methylammonium chloride was equal to 79·6 per cent. of the weight
of ammonium chloride which had entered into reaction. When the
value of the by-products is taken into consideration, it will be seen
that the methylammonium salt is obtained for a very small outlay.

Preparation of Dimethylammonium Chloride.

The formation of the above salt in this reaction has been recently
pointed out by Knudsen (*loc. cit.*), but the method adopted for its
preparation distinctly shows the absence of a reasonable apprecia-
tion of the probable mechanism of the changes. Thus, in an experi-
ment designed with the object of obtaining the best yield of the
secondary amine, a useless, not to say a wasteful, excess of form-
aldehyde was employed without any particular advantage. The
following experiment, carried out on the lines of the present theory,
gave a very good result.

Expt. II.—Two hundred grams of ammonium chloride and 400
grams of formalin were heated to 104°, as in Expt. I, and 65 grams
of ammonium chloride were recovered. To the filtrate 300 grams
of formalin were now added, and the solution was again heated at
this stage to 115°, and maintained as nearly as possible at this tem-
perature until no more liquid distilled. This required about three
and a-half hours. Since methylammonium chloride, produced
during the first stage, is less easily dissociated than ammonium
chloride, a higher temperature was required to bring about reac-
tion (3). It was noticed that whilst a volatile liquid commenced
to distil at about 52° in the first stage, 92° was reached in the
second stage before any liquid distilled, which is quite in agreement
with theory.

The product was concentrated by evaporation at 100° until a
scum appeared on the surface of the hot liquid ; 7 grams of ammon-

ium chloride, and 27 grams of pure methylammonium chloride were recovered from the material which had separated after cooling. The product was now heated to 120°, until a portion when cooled became a semi-solid, crystalline mass, after which it was allowed to remain for two days in a partial vacuum over sodium hydroxide. It was then treated with chloroform as described under Expt. I, and 122 grams of nearly pure dimethylammonium chloride (Found, Cl = 43·14. Calc., Cl = 43·5 per cent.) were ultimately obtained. The final residue contained some trimethylammonium chloride, but was not further dealt with.

The yield of dimethylammonium chloride calculated on the weight of ammonium chloride which had entered into reaction (that is, $200 - 72 = 128$ grams) was therefore 95·3 per cent. with the use of 700 grams of formaldehyde solution. Knudsen obtained a yield of 70 per cent. from 100 grams of ammonium chloride and 1000 grams of formalin.

Production of Trimethylammonium Chloride from the Interaction of Formaldehyde and Dimethylammonium Chloride.

In order to prove the origin of trimethylamine, in accordance with the present theory, the following experiment was made.

Expt. III.—Dimethylammonium chloride (20·5 grams) and 45 grams of a solution of formaldehyde (molecular ratio 1 : 2) were heated in a distillation flask to 110° for four hours. The composition of the distillate, which weighed 18 grams, is given under III (p. 846). The product, after concentration as far as possible by evaporation at 100°, was heated to 120°, after which it was allowed to remain over sodium hydroxide, as in Expt. II. The residue was dissolved in chloroform, and on addition of ether (well dried) 4·5 grams of crystals were precipitated, which contained Cl = 36·93 (C_3H_9N,HCl requires Cl = 37·17 per cent.).

A platinichloride was prepared, which contained Pt = 37·03 (C_3H_9N,H_2PtCl_6 requires Pt = 36·95 per cent.).

The residue, after removal of the solvent, was distilled with a 40 per cent. potassium hydroxide solution; the alkaline distillate, which possessed a strong odour of formaldehyde, was easily proved to consist chiefly of dimethylamine with only a small proportion of the tertiary base. The original reaction product, tetramethyl-methylenediamine hydrochloride, was readily hydrolysed when heated with a solution of potassium hydroxide, thus,

$$CH_2(NMe_2)_2,2HCl + 2KOH = CH_2O + 2NHMe_2 + 2KCl + H_2O.$$
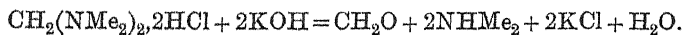
The small yield of trimethylamine was due to the relatively low temperature attained during the process.

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Expt. IV.—The above was repeated, but the temperature was raised to 160°, after evaporation at 100°; a yield of 14 grams of trimethylammonium chloride was obtained, thus proving the origin of the tertiary base, as shown in the scheme, equation (6).

Behaviour of Methylammonium Chloride and Formaldehyde in the Presence of Ethyl Alcohol.

According to theory, no methylammonium chloride should result from the interaction of ammonium chloride and formaldehyde in the absence of water, a point which is not suggested by such an equation, as $2CH_2O + NH_3 = CH_3 \cdot NH_2 + H \cdot CO_2H$, which is given by Knudsen to show the formation of methylamine. The insolubility of ammonium chloride in pure alcohol presents a difficulty in the use of this salt; however, the test has been made with the methyl derivative.

Expt. V.—Seventeen grams of methylammonium chloride and 15 grams of paraformaldehyde (2 mols.) were heated with 50 c.c. of alcohol under reflux. The aldehyde was rapidly depolymerised and a clear, homogeneous solution was obtained as soon as the boiling point of alcohol was reached. After a short time the liquid gradually separated into two layers, and the change was completed after one hour. The lower layer when cold was a semi-solid, crystalline mass, from which 10·5 grams of methylammonium chloride were recovered.

The supernatant liquid was shaken with a saturated aqueous solution of calcium chloride, dried, and distilled; 46 grams of ethylal (b. p. 88—89°) were obtained, which was equal to 88·4 per cent. of the theoretical from 15 grams of formaldehyde. When molecular proportions of methylammonium chloride (17 grams) and paraformaldehyde (7·5 grams) were used, 13·5 grams of the amine salt were recovered, and 20 grams of ethylal were obtained.

No dimethylammonium chloride was formed, which bears out the part played by water in the general reaction.

Interaction of Formaldehyde and Ammonium Chloride in the Presence of Water alone.

It was pointed out, in the results given under Expt. I, that the yield of methylammonium chloride was equal to 79·6 per cent. of the weight of ammonium chloride which had entered into reaction. Theoretically, from equations (1) and (2) one molecular proportion of ammonium chloride should yield one of methylammonium chloride, that is, 126·1 parts of the latter salt from 100 parts of the former. With the use of commercial formalin there is inevitable

loss of formaldehyde as methylal, which, for obvious reasons, cannot be profitably counteracted by using an excess of the aldehyde solution. This loss of aldehyde is undoubtedly one of the factors that affects the ultimate yield of methylamine; when it was eliminated by the use of paraformaldehyde, a larger yield of the amine was obtained.

Expt. VI.—Twenty-seven grams of ammonium chloride, 30 grams of paraformaldehyde (molecular ratio 1:2), and 80 c.c. of water were gradually heated. At 80° a clear solution was obtained, and the temperature was maintained for four hours at 104°. Slightly more than one-third (9·06 grams) of the ammonium chloride was recovered, whilst 18·96 grams of pure methylammonium chloride were obtained. This equals 105·6 parts from 100 parts of ammonium chloride. The amount of dimethylammonium chloride produced was not estimated. It is not suggested from the results of this experiment that paraformaldehyde could be economically used on a large scale with advantage, since, quite apart from its relatively high cost, neither formic acid nor part of the unchanged aldehyde can be recovered as by-products. The experiment has served to support the views put forward, and perhaps on a small scale may have some advantage.

Many other points, dealing chiefly with the identification of the intermediate products, which have not been touched upon in the present paper, will be elaborated in a future communication.

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LXXIII.—*The   Liberation   of   Hydrogen   Sulphide from Gob Fires in Coal Mines.*

By THOMAS JAMES DRAKELEY.

EXPERIMENTS described in an earlier paper (T., 1916, **109**, 723) have shown that iron pyrites favourably influences to a small extent the oxidation, and therefore spontaneous ignition, of coal.

Lewes (Second Report of the Royal Commission on Coal Supplies, 1904 [Cd. 1991], Vol. 2, 232), however, expressed the view that iron pyrites has no connexion whatever with the spontaneous heating of coal. This inference is based on the fact that, in an inspection of a case of spontaneous combustion where the coal was heated, the sulphur was found to be evolved as hydrogen sulphide

and not as sulphur dioxide, as would have been the case "if the pyrites had anything to do with" the fire.

The fact that hydrogen sulphide is evolved during the initial stages of a gob fire is indisputable; but the assumption that if iron pyrites favoured the heating, the sulphur would be given off necessarily as sulphur dioxide appeared to need verification. There is the reasonable possibility that the sulphur dioxide may be reduced to hydrogen sulphide by contact with the heated coal.

Experiments were conducted to investigate this question, and a detailed account is given in the following pages.

The investigation has shown that hydrogen sulphide may be formed from heated coal and iron pyrites in a number of ways, as, for example, by heating coal, by passing sulphur dioxide over heated coal, by heating mixtures of coal with sulphur or iron pyrites, by passing water vapour or hydrogen over heated iron pyrites, etc.

Therefore, at the seat of a gob fire, it would appear to be quite possible for sulphur dioxide to be formed, but, previous to an external outbreak of the fire, there would be very little likelihood of this sulphur dioxide being liberated into the mine atmosphere. If the sulphur dioxide were not reduced completely to hydrogen sulphide by contact with heated coal in the immediate vicinity of the fire, it would encounter the larger volumes of hydrogen sulphide that would be issuing from the gradually heated material in the locality, and thereby would be decomposed to give sulphur. In consequence of such reactions, no sulphur dioxide would reach the external air.

In view of this, Lewes's statement, that if iron pyrites assisted in the ignition of the coal the sulphur would be liberated as sulphur dioxide, seems to be erroneous.

The Formation of Hydrogen Sulphide by Passing Sulphur Dioxide over Heated Coal.

In order to reproduce to a certain extent the conditions of the liberation of the gas from the gob, a moist mixture of four volumes of carbon dioxide and one volume of sulphur dioxide was passed over 20 grams of powdered coal contained in a glass tube. The tube (45 cm. long and 2 cm. in diameter) was gradually heated in a 28 cm. platinum-wound electric furnace until the temperature reached 500°. The temperature was maintained at 500° until no further evolution of gas from the coal could be detected. During this time, the mixture of carbon dioxide and sulphur dioxide was passed over the coal at the rate of 2 litres per hour.

The gases evolved were delivered, first, into a Woulfe's bottle, where tarry oils were deposited, through a spiral tube immersed in water at 10°, and then through pure concentrated sulphuric acid.

After this treatment, the hydrogen sulphide in the gases was absorbed by passing them through a train of four bottles, each containing a solution of copper sulphate acidified with hydrochloric acid. A duplicate absorption train was arranged so that by means of a three-way tap the gases could be diverted from one train to the other.

At the commencement of an experiment, the air in the glass tube in the furnace was displaced by a stream of carbon dioxide. The heating was started, and the mixture of carbon dioxide and sulphur dioxide was passed through the tube. At first, no precipitate appeared in the copper sulphate solution, but as soon as the slightest trace was discernible the tap was turned so that the gases were washed with fresh copper sulphate solution in the second absorption train. This was to eliminate any possible errors that might arise from a reaction between the hydrogen sulphide and any soluble gases with which the copper sulphate solution had been contaminated during the initial stage of the experiment.

After the temperature of the furnace had been 500° for about two hours, the mixture of carbon dioxide and sulphur dioxide was turned off to test whether the evolution of volatile products was continuing. When this ceased, the precipitated copper sulphide was collected, washed, dried, and detached from the filter paper. The filter paper was ignited, and the ash was added to the main part of the precipitate, which was mixed with sulphur, heated to redness in an atmosphere of coal gas, cooled, and weighed.

From the weight of cuprous sulphide, the quantity of sulphur evolved as hydrogen sulphide was calculated.

Blank experiments (in which only carbon dioxide was passed over the coal) were made for each sample of coal.

Three samples of different coals were used in the experiments.

Coal " A " was a selected sample of Arley coal from a local colliery. The coal was black, possessing considerable lustre and a brown streak. It fractured along lines chiefly defined by "mother of coal " (charcoal). The seam is not subject to spontaneous combustion. The sample was picked carefully, and all visible impurity excluded.

Coal " B " was a selected sample of "Five Feet " coal from a colliery near Chester. The coal was moderately dull black, and was exceptionally close and compact. The fracture was mainly splinty. From its properties it would appear to be a canneloid

coal. The seam is not subject to gob fires. The sample was freed carefully from all visible impurity.

Coal " C " was from a local colliery, and was a deliberately chosen inferior sample from the Ravine Seam, which is subject to spontaneous combustion. The coal consisted of alternate lustrous black and comparatively dull black layers; it fractured easily along planes which contained considerable deposits of calcium carbonate. Iron pyrites was present in the finely disseminated form. The sample was obtained from the neighbourhood of a gob fire.

Analyses of the coals gave the following results:

Estimation.	Coal " A."	Coal " B."	Coal " C."
Specific Gravity.	1·248.	1·247.	1·341.
Ultimate Analysis :—	Per cent.	Per cent.	Per cent.
Carbon	80·937	75·761	67·730
Hydrogen	4·815	5·783	2·992
Nitrogen	1·365	1·487	1·015
Sulphur	1·412	0·953	4·017
Ash	1·660	3·646	12·084
Oxygen, etc. (by diff.)	9·811	12·350	12·162
	100·000	100·000	100·000
Proximate Analysis :—			
Fixed Carbon	66·475	47·606	51·637
Ash	1·660	3·646	12·084
Moisture	0·828	0·566	3·738
Volatile matter	31·037	48·182	31·541
	100·000	100·000	100·000
Yield of Volatile Matter on heating to 500°	14·421	25·830	20·516

The results of the experiments are given in the accompanying table, and are calculated for a weight of 100 grams.:

Result.	Sample.	Time. Mins.	Weight of sulphur in coke residue. Grams.	Weight of sulphur evolved as H_2S. Grams.
1		30	1·352	0·032
2		60	1·351	0·035
3	Coal " A."	30	1·373	0·172
4		60	1·379	0·194
5		30	0·618	0·049
6		60	0·609	0·049
7	Coal " B."	30	0·711	0·316
8		60	0·703	0·351
9		30	2·878	1·096
10		60	2·879	1·098
11	Coal C."	30	4·186	2·065
12		60	4·205	2·619

In the above table, each result represents the average of five experiments.

The time mentioned in the second column gives the number of minutes taken to raise the temperature of the furnace from 15° to 500°. Subsequently, the temperature of the furnace was maintained at 500° until the end of the experiment, which occupied from two to two hours and a-half.

Results 1—4 were obtained with coal " A," 5—8 with coal " B," and 9—12 with coal " C." Results 1, 2, 5, 6, 9, 10 were blank determinations, and give the weight of sulphur that was eliminated as hydrogen sulphide when 100 grams of the coal were heated in a current of moist carbon dioxide. Results 3, 4, 7, 8, 11, 12 were obtained by passing the mixture of carbon dioxide and sulphur dioxide over the heated coal.

In the blank experiments, the temperature of the furnace reached the following values before any appreciable quantity of hydrogen sulphide was evolved from the samples of coal.

	Coal " A."	Coal " B."	Coal " C."
Temperature	290°	270°	275°

It was observed, however, that when the mixture of carbon dioxide and sulphur dioxide was passed over the coal, no hydrogen sulphide was evolved until a much higher temperature had been reached. The values are given below.

	Coal " A."	Coal " B."	Coal " C."
Temperature	440°	435°	445°

During this time, the coal in the tube appeared to have become coated with a whitish-yellow powder. No doubt this was a slight deposit of sulphur which, probably, had been formed by the reaction between the sulphur dioxide passing over and the hydrogen sulphide evolved from the coal. Possibly the organic tarry liquids from the coal may have influenced the interaction of the hydrogen sulphide and the sulphur dioxide (compare Klein, *J. Physical Chem.*, 1910, **15**, 1, who also showed that water was a catalyst).

When the temperature of the furnace reached about 450°, the evolution of hydrogen sulphide became so rapid that the stream of sulphur dioxide was insufficient to react with it completely, and a rapid precipitation of copper sulphide occurred.

It may be noted that a deposit of sulphur is observed frequently in the initial stages of an actual occurrence of a gob fire (compare Henshaw, Departmental Committee on Spontaneous Combustion in Coal Mines, Minutes of Evidence, 12th Feb.—16th July, 1913, p. 26); but this slight yellow deposit in the cracks of the coal, where the heating is evidenced, may be due, in addition, to other causes than the one stated above. However, the similarity between the actual gob fire and the experiment was striking.

The percentage of sulphur in the coke residue, which was slightly more friable when sulphur dioxide was passed over the coal, would indicate that a quantity of the sulphur becomes fixed in the coke. This may be due to an interaction between the sulphur dioxide and the ash constituents.

It is possible that if the mineral matter of the coal contained lime at 500°, a little sulphur may have been formed by the action of the sulphur dioxide on the lime (Veley, T., 1893, **63**, 821; compare Hammick, this vol., 379).

The results indicate that the evolution of the hydrogen sulphide is increased where sulphur dioxide is passed over heating coal. The observed fact that the sulphur is evolved as hydrogen sulphide and not as sulphur dioxide from a gob fire does not, therefore, decide the question whether or not iron pyrites assists in the spontaneous ignition of coal.

The Formation of Hydrogen Sulphide by Heating Mixtures of Coal and Sulphur.

From the results obtained in the previous section, it would appear that the production of hydrogen sulphide resulted from heating the coal with the sulphur which previously had been deposited upon it. To investigate this question, mixtures of 20 grams of coal with various proportions of sulphur were heated in a glass tube in an electric furnace to 500°.

In the first series of experiments a stream of moist carbon dioxide was passed through the tube, and was interrupted only to test whether all the volatile gases had been liberated from the coal.

In the second series of experiments, the air was displaced from the glass tube containing the mixture of coal and sulphur by means of a stream of dry carbon dioxide. The carbon dioxide was turned off until all volatile matter had been expelled from the mixture, then the residual gases were swept into the absorption train by means of the current of dry carbon dioxide.

Dry carbon dioxide was driven regularly over the heated mixtures in the experiments comprising the third series. The current of carbon dioxide was interrupted only to test for the cessation of the evolution of gas from the mixtures.

The apparatus and the method of collecting the hydrogen sulphide have been described in the previous part of the paper.

The following table gives the weight (in grams) of sulphur that was eliminated as hydrogen sulphide and the weight of sulphur in the coke from mixtures of 100 grams of coal with different quantities of sulphur:

Result.	Sample.	Weight of sulphur mixed with 100 grams of coal. Grams.	Series 1.		Series 2.		Series 3.	
			S in coke. Grams.	S as H_2S. Grams.	S in coke. Grams.	S as H_2S. Grams.	S in coke. Grams.	S as H_2S. Grams.
1	Coal " A."	0	1·352	0·032	1·361	0·031	1·363	0·031
2		1	1·373	0·801	1·394	0·605	1·394	0·515
3		2	1·374	1·652	1·401	1·151	1·391	0·997
4		3	1·371	2·302	1·393	1·572	1·404	1·354
5		4	1·379	3·109	1·402	2·095	1·395	1·736
6		5	1·370	4·036	1·401	2·097	1·397	1·831
7		6	1·373	4·783	1·395	2·103	1·403	1·987
8	Coal " B."	0	0·608	0·049	0·618	0·049	0·619	0·049
9		1	0·613	0·872	0·617	0·693	0·623	0·604
10		2	0·618	1·801	0·835	1·502	0·871	1·025
11		3	0·617	2·673	1·201	1·712	1·114	1·513
12		4	0·615	3·397	1·439	2·383	1·503	2·007
13		5	0·612	4·413	1·423	2·524	1·501	2·188
14		6	0·617	5·216	1·457	2·591	1·512	2·436
15	Coal " C."	0	2·877	1·098	2·878	1·097	2·905	1·097
16		1	3·054	1·897	3·082	1·803	3·085	1·802
17		2	3·236	2·633	3·298	2·516	3·284	2·517
18		3	3·509	3·189	3·611	3·167	3·627	3·091
19		4	3·605	4·314	3·828	3·591	3·971	3·388
20		5	3·892	4·846	3·909	3·807	4·426	3·645
21		6	3·955	5·684	4·136	4·070	4·518	3·923

It is well known that sulphur below its boiling point combines with hydrogen, and when heated to 200° reacts with paraffin or vaselin, forming hydrogen sulphide. Even if little free hydrogen is evolved from coal at 500°, the action of sulphur on bituminous coal would explain the production of hydrogen sulphide.

Evidence that the coal behaved differently when heated with sulphur was noted by the change in the character of the coke.

When coal " A " was heated alone to 500°, a firm, hard coke with submetallic lustre was produced, but as the quantity of sulphur admixed with the coal increased, the coherence of the coke residue diminished. Indeed, in the experiments of series 1, when the coal was heated with 6 grams of sulphur, the resulting coke was quite pulverulent. The cokes were less powdery in series 2 than in series 1, and in series 3 than series 2. The above statements were true also for coals " B " and " C."

The influence of moisture on the production of hydrogen sulphide was particularly noticeable (compare Jones, *Mem. Manchester Phil. Soc.*, 1904, **48**, No. XVI.). In the experiments in series 1, in which moisture was admitted, the sulphur evolved as hydrogen sulphide exceeds the quantity collected in the corresponding experiments in series 2 and 3. In series 3, dry carbon dioxide was passed continually over the mixtures, and the production of hydrogen sulphide was the smallest.

It is impossible, however, to state definitely how far moisture is responsible for the formation of hydrogen sulphide, as water is one of the decomposition products on heating coal, and therefore its elimination is incapable of being accomplished. That it is a very important factor is demonstrated by the greater production of hydrogen sulphide in series 1 than in either series 2 or 3. Furthermore, with coal " C," which contained more than 3 per cent. of moisture, the difference between the results in series 2 and 3 and those in series 1 is not so marked as with the comparatively dry coals " A " and " B." That moisture is probably not the sole factor is substantiated by the production of hydrogen sulphide on heating such a mixture as sulphur and paraffin.

The decomposition of the moisture by the heated sulphur would produce oxygen and hydrogen sulphide, and the loss of the caking power would appear to be explained satisfactorily as the result of the oxidation to inert substances of those particular compounds which endow the coal with this property. This was upheld by the fact that the coke increased in hardness from series 1 to 3, that is, as the moisture admitted to the reaction was diminished. No attempt was made to determine whether any carbon dioxide was reduced by the heated coal to carbon monoxide (see Meyer and Schuster, *Ber.*, 1911, **44**, 1931).

The weight of sulphur fixed in the coke showed no marked variation with the different mixtures containing coal " A "; but the cokes from coals " B " and " C " exhibited a gradually increasing fixation of sulphur. The presence of moisture tends to reduce the quantity of sulphur left in the coke.

During each experiment there accumulated a precipitate of sulphur in the sulphuric acid wash-bottle. This was noticeable particularly with the coal mixtures containing the larger quantities of sulphur. At the conclusion of an experiment the sulphuric acid was found to emit a pungent and disagreeable garlic-like odour.

The experiments indicate that where mixtures of sulphur and coal are heated, the sulphur is evolved largely as hydrogen sulphide and that its formation is increased by the presence of moisture.

These conditions are fulfilled admirably during the initial stage of a gob fire; for sulphur becomes mixed with the coal, moisture is present, and the temperature gradually rises. Therefore it is not surprising that hydrogen sulphide is liberated from the gob and that sulphur dioxide is not observed until the fire breaks externally. Incidentally, the author may add that he has been assured by one who has had experience of gob fires that the odour produced in the room by heating coal with sulphur is almost identical with the peculiar and characteristic " gob stink."

Hence it may be argued that such a series of reactions as the following take place in the gob. First, iron pyrites assists the ignition and liberates sulphur dioxide. The materials in the locality are heated and evolve hydrogen sulphide, which reacts with the sulphur dioxide to form sulphur. The sulphur is deposited on the coal which is being heated gradually, and from this mixture the sulphur is disengaged as hydrogen sulphide.

It certainly cannot be inferred that iron pyrites has no influence on the spontaneous ignition merely because hydrogen sulphide, and not sulphur dioxide, is liberated from the gob.

The Formation of Hydrogen Sulphide by Heating Mixtures of Coal and Iron Pyrites.

The experiments in this section were made in the same manner as those just described. The mixtures of coal and iron pyrites were heated in a glass tube in an electric tube furnace to 500°. Previous to the heating, the air was displaced from the tube by a stream of carbon dioxide, whilst at the conclusion the residual gases were swept into the absorption train, containing acidified copper sulphate solution, by again turning on the current of carbon dioxide.

The analysis of the iron pyrites gave the following results:

Silica	1·416 per cent.	
Iron	45·902	,, ,,
Sulphur	51·978	,, ,,
Copper	trace	

The weight of sulphur evolved as hydrogen sulphide from various mixtures of coal and iron pyrites is given in the accompanying table.

Result.	Sample.	Weight of iron pyrites mixed with 100 grams of coal. Grams.	Weight of sulphur evolved as hydrogen sulphide. Grams.
1		0	0·031
2		2	0·208
3		4	0·387
4	Coal " A "	6	0·533
5		8	0·666
6		10	0·876
7		0	0·049
8		2	0·604
9		4	0·685
10	Coal " B "	6	0·789
11		8	0·901
12		10	1·013
13		0	1·089
14		2	1·620
15		4	1·953
16	Coal " C "	6	2·194
17		8	2·576
18		10	3·058

Hence, the liberation of hydrogen sulphide from a gob fire may be due, to a certain extent, to the effect of the coal being heated in the presence of iron pyrites.

The Formation of Hydrogen Sulphide by Passing Moist Carbon Dioxide over Heated Iron Pyrites.

A stream of dried carbon dioxide was passed over iron pyrites heated as in the previous experiments to 500° in an electric tube furnace, and no hydrogen sulphide could be detected in the issuing gases.

When, however, a current of moist carbon dioxide was passed over the heated iron pyrites it resulted in the immediate production of hydrogen sulphide (compare Jones, *loc. cit.*). A considerable accumulation of sulphur collected in the cooler parts of the glass tube.

This experiment indicates that some of the hydrogen sulphide liberated from a gob fire may owe its origin to the action of moisture on heated iron pyrites. In the gob there would be oxidisable material, which would acquire with avidity the oxygen produced by the decomposition of the moisture, and would thereby tend to promote the formation of the hydrogen sulphide.

The Formation of Hydrogen Sulphide by Passing Hydrogen over Heated Iron Pyrites.

For the experiments in this part 2 grams of iron pyrites were placed in each of two tubes (48 cm. long and 1 cm. in diameter), which were introduced simultaneously into an electric tube furnace at 500°. Through one tube was passed a stream of dry hydrogen at the same rate as moist hydrogen was driven through the other.

The gases leaving the tube were delivered direct into acidified copper sulphate solution. The precipitated copper sulphide was collected every fifteen minutes, and the sulphur estimated as previously described.

The quantity of sulphur emitted as hydrogen sulphide is given in the following table [under (*a*) when dry hydrogen was passed,

Time.	Sulphur evolved as hydrogen sulphide	
	(*a*)	(*b*)
Minutes.	Grams.	Grams.
15	0·436	0·779
30	0·608	1·140
45	0·705	1·388
60	0·753	1·518
75	0·773	1·590
90	0·792	1·628
105	0·796	1·632
120	0·801	1·636

under (*b*) when wet hydrogen was used. The results are calculated for a weight of 10 grams of iron pyrites.]

The values clearly demonstrate the paramount importance of moisture in the reduction of iron pyrites by hydrogen.

In the coal mine the gob may reach a high temperature when hydrogen will form a considerable proportion of the gases emitted from the coal (Burgess and Wheeler, T., 1910, **97**, 1917).

In these circumstances, should it pass over heated iron pyrites, hydrogen sulphide would constitute one of the gases emitted from the gob.

The author's thanks are due to Mr. George William Farmer for assistance in the last series of experiments.

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WIGAN.   [*Received, July 14th,* 1917.]

LXXIV.—*The Constitution of Carbamides. Part IV. The Mechanism of the Interaction of Urea and Nitrous Acid.*

By EMIL ALPHONSE WERNER.

THE decomposition of urea by nitrous acid is generally considered to be properly expressed by the following simple equation:

$$CON_2H_4 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O,$$

and this reaction is frequently cited in text-books as additional evidence in support of the " carbamide " structure of urea.

Theoretically, this reaction should be available for the estimation of urea, as is commonly suggested in the literature; it is never used for this purpose, and it is doubtful whether it ever has been, since experiment has proved it to be quite valueless. On the other hand, it constitutes a well-known method for the estimation of nitrous acid, with a very fair degree of accuracy, on the supposition that the above equation is true. No doubt for this reason, and on account of the employment of other methods for the estimation of urea, this reaction has been considered all along as a normal change, scarcely deserving of any further investigation.

In continuation of the author's work on the constitution and properties of urea, its behaviour towards nitrous acid has been submitted to a careful quantitative study. The following are some of the more important facts which have been observed, and whilst they

show what an erroneous conception has been generally entertained regarding the nature of this reaction, they fully justify the necessity for a proper investigation into the true mechanism of the change.

1. Urea and pure nitrous acid in aqueous solution did not interact. (Expts. IX, X.)

2. The presence of a strong acid (hydrochloric or nitric) quickly promoted a brisk interaction, even in dilute solutions, and the reaction was completed in a relatively short time.

3. The presence of a weak acid, such as acetic acid, did not promote an interaction, unless the concentration was abnormally high, and even then the velocity of the reaction was extremely slow.

4. The volume of nitrogen evolved was not a direct measure of the amount of urea decomposed, calculated on the basis of the above equation; the quantity decomposed was much greater * than that indicated by the evolved nitrogen.

5. Only when urea was present in considerable excess was the volume of nitrogen evolved an approximately true estimate of the amount of nitrous acid decomposed.

6. The volume ratio of carbon dioxide to nitrogen (1 : 2) required by the equation has never been obtained; the proportion of carbon dioxide was always much higher; moreover, the composition of the gas was liable to much variation with small changes in concentration.

It is obvious that, so far as the usual explanation of this reaction is concerned, all these facts stand out as anomalies for which the ordinary equation offers no explanation.

Now, anomalies in such a reaction can have no reality; their apparent existence is the natural consequence of an erroneous conception of the change, and when the true constitution of urea is considered they appear as normal phenomena which reveal the true mechanism of the interaction.

Mechanism of the Interaction of Urea and Nitrous Acid.

In the course of a recent investigation on the properties of pure nitrous acid, Rây, Dey, and Ghosh (this vol., p. 414) noticed that a solution of the acid ($N/32$-HNO_2) was practically without action on urea, "no matter how much urea was added." They found that the addition of sulphuric acid was necessary to promote and complete a reaction. This anomaly, they remark, "was without any apparent reason," a just comment when urea is believed to be carbamide. Pure nitrous acid in aqueous solution does not react with

urea until an amino-group is presented for attack, a condition brought about by the production of a salt of urea on the addition of a sufficiently strong acid, thus:

$$HN:C\!<^{NH_3}_O + HX = HN:C\!<^{NH_2,HX}_{OH}.$$

The first stage of the reaction then takes place, in accordance with the equation *:

(a) $HN:C\!<^{NH_2,HX}_{OH} + HNO_2 = N_2 + HNCO + 2H_2O + HX.$
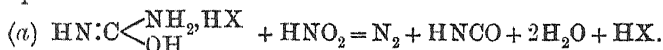
The cyanic acid is decomposed in two ways as fast as it is generated. It is hydrolysed,† thus:

(b) $HNCO + H_2O = NH_3 + CO_2,$

and directly attacked by nitrous acid, according to the equation:

(c) $HNCO + HNO_2 = CO_2 + N_2 + H_2O$ (see Expts. VII and VIII).
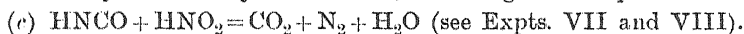
Both these decompositions proceed simultaneously with the primary reaction (a), but the relative proportions in which they take place can be varied at will, within certain limits, by adopting suitable conditions which will be presently shown.

The production of cyanic acid has been easily demonstrated by its isolation in the form of the silver salt; thus when urea was attacked by nitrous acid in the presence of silver nitrate and a small excess of nitric acid, a yield of pure silver cyanate was obtained equal to 42 per cent. of the theoretical, calculated on the equation:

(d) $HN:C\!<^{NH_2,HNO_3}_{OH} + HNO_2 + AgNO_3 =$
$$N_2 + AgOCN + 2HNO_3 + 2H_2O.$$
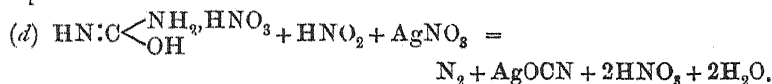
Considering the favourable conditions for hydrolysis, and the very sensible solubility of silver cyanate in dilute nitric acid, such a result was even more successful than could reasonably have been expected.

It will be seen now that when urea (in the form of a salt) and nitrous acid interact, a certain proportion of nitrogen from the urea is always fixed as an ammonium salt, and herein lies the fallacy of the reaction, so far as the estimation of urea is concerned.

The variations observed in the ratios of carbon dioxide to nitrogen are thus easily explained, since the volume of nitrogen evolved is lowered in proportion to the amount of cyanic acid hydrolysed. The latter change can be only partly suppressed, even under the

* No doubt this decomposition originates through the medium of diazotisation.

† Cyanic acid in water alone is hydrolysed to urea, $2HNCO + H_2O = CON_2H_4 + CO_2$ (Normand and Cumming, T., 1912, **101**, 1859); in the presence of mineral acid, of course, the change is as above.

most favourable conditions (that is, high concentration and nitrous acid in excess), with the result that the ratio of carbon dioxide to nitrogen evolved is never that which has been erroneously assumed.

Now, according to the above explanation, the interaction of urea and nitrous acid is theoretically clearly divisible into two stages, during the first of which one molecule of urea is completely decomposed by one molecule of nitrous acid, instead of by two molecules, as has been commonly, but falsely, supposed.

This has been easily proved experimentally, by adopting the exact conditions which the theory rigorously demands, namely, (1) the presence of urea in excess at the outset, (2) a low concentration of nitrous acid, (3) the presence of mineral acid in excess of that required to neutralise ammonia generated from the hydrolysis of cyanic acid, and so to maintain the proper configuration of the urea molecule. Under these conditions the decomposition of cyanic acid by nitrous acid can be almost completely suppressed in favour of its decomposition by hydrolysis.

A knowledge of the amount of cyanic acid hydrolysed, compared with the volume of nitrogen evolved, is an all-important factor, by means of which a very clear insight into the mechanism of the reaction has been obtained.

The following results illustrate the degree of success which has been realised in experimentally proving the problem which is indicated by the theory of the change now put forward.

TABLE I.

	I. $CON_2H_4 + HNO_2.$	II. $CON_2H_4 + HNO_2.$	III. $CON_2H_4 + HNO_2,$
Molecular ratios	1 : 1	1·5 : 1	2 : 1
Nitrogen evolved, calculated on the theoretical	92·5 per cent.	95·73 per cent.	99·34 per cent.
HNCO hydrolysed	87·0 ,,	96·0 ,,	99·5 ,,
HNCO decomposed by HNO_2	13·0 ,,	4·0 ,,	0·5 ,,
Proportion of urea actually decomposed by one molecule of HNO_2	79·5 ,,	91·73 ,,	98·84 ,,
Composition of gas evolved	$CO_2 = 43·1$,, $N_2 = 53·6$,, $NO = 3·2$,,	$CO_2 = 43·2$,, $N_2 = 54·5$,, $NO = 2·2$,,	$CO_2 = 44·2$,, $N_2 = 54·3$,, $NO = 1·3$,,
Ratio CO_2 to N...	1 : 1·24	1 : 1·26	1 : 1·22

It will be seen, on viewing the results of the above experiments (the full details of which are given under Expts. V., VII., and

VIII.), that the amount of urea decomposed by one molecular proportion of nitrous acid, according to the equation

$$HN:C{\displaystyle <_{OH}^{NH_2,HX}} + HNO_2 = N_2 + HNCO + 2H_2O + HX$$
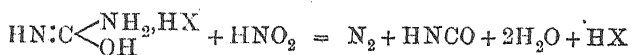
was less than that indicated by the volume of nitrogen evolved. The difference was most marked when the exact proportions (equal molecules) of urea and nitrous acid required by the equation were used, since the conditions were less favourable for a quantitative realisation of the second change, namely,

$$HNCO + H_2O + HX = NH_4X + CO_2,$$
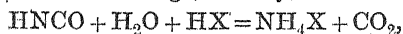
than when a considerable excess of urea was present. In the latter case, the desired object was almost fully attained (III), and the true nature of the primary stage of the reaction thereby established.

As regards the composition of the evolved gases, the ratio of carbon dioxide to nitrogen was in each case approximately $1:1\cdot20$; this, of course, was not the true value, since a very sensible amount of carbon dioxide was held in solution in the residual liquid; when corrected, in the case of result III, for example, the true ratio was $CO_2 = 1$, $N = 1\cdot02$, or $1:1$ as required by the combination of the two equations.

It may be well to direct attention here to the constant presence of a small amount of nitric oxide in the evolved gas; whilst this was no doubt due to the decomposition of a corresponding proportion of nitrous acid, thus, $3HNO_2 = HNO_3 + H_2O + 2NO$, it was not found possible to eliminate it completely, even when urea was in excess and the concentration of nitrous acid, at the outset of the reaction, was as low as $N/20$. Under such conditions as are commonly adopted, in the estimation of nitrous acid by the aid of urea, the proportions of nitric oxide may easily amount to between 6 and 8 per cent. of the evolved gases, according to the particular concentration of the solution used. This fact appears to have been generally overlooked.

It is obvious when the ratios $HNO_2:N$ and $3HNO_2:2NO$ are compared that the presence of nitric oxide must lead to a result in excess of the true value; for example, in the case of result III, table I, if the nitric oxide found was included as nitrogen, the yield of the latter would appear as $101\cdot8$ per cent. of the theoretical.

Rây and his co-workers (*loc. cit.*), using a solution of nitrous acid of concentration $N/32$, obtained a result which they found was in excess of the true value in nearly the same proportion as above, and no doubt for the same reason. This decomposition of

nitrous acid readily explains why a solution of comparatively high concentration, say $HNO_2 = N/6$, can slowly attack urea; the generation of nitric acid gradually brings about the required condition.

The results under table I were obtained by adding the theoretical proportion of nitrous acid slowly and at intervals to the acid solution of urea. A very low concentration of nitrous acid was thus ensured throughout the progress of the reaction.

When the molecular proportion of nitrous acid was added all at once, the concentration at the outset being $HNO_2 = N/6$, the results, as was to be expected, were very different, as shown below (Expts. IV. and V.).

TABLE II.

	I. $CON_2H_4 + HNO_2$. 1 : 1	II. $CON_2H_4 + HNO_2$ 1·5 : 1	III. $CON_2H_4 + HNO_2$ 2 : 1
Molecular ratios			
Nitrogen evolved	91·46 per cent.	94·40 per cent.	96·48 per cent.
HNCO hydro-lysed..............	71·5 ,,	74·5 ,,	76·0 ,,
HNCO decomposed by HNO_2	28·5 ,,	25·5 ,,	24·0 ,,
Urea actually decomposed by HNO_2	62·96 ,,	68·90 ,,	72·48 ,,
Composition of $\left\{\begin{array}{l}\\\\\\\end{array}\right.$ gas evolved	$CO_2 = 36·5$,, $N_2 = 59·2$,, $NO = 4·2$,,	$CO_2 = 37·8$,, $N_2 = 59·08$,, $NO = 3·06$,,	$CO_2 = 43·6$,, $N_2 = 54·1$,, $NO = 2·2$,,

Whilst the volume of nitrogen evolved was only slightly below that previously observed, the amount of urea decomposed was, in each case, much less than before. This was the natural result of the much greater facility offered for the decomposition of cyanic acid by nitrous acid at the higher concentration. The latter was also responsible for the slight increase in the proportions of nitric oxide. The constancy * to be observed in the proportions of carbon dioxide and nitrogen in the evolved gases, as shown in both tables, in spite of the fairly wide differences in the proportions of urea decomposed, is easily explained when the ratios of cyanic hydrolysed to cyanic decomposed by nitrous acid are considered.

As regards the very slow reaction which was noticed to take place between urea and nitrous acid in the presence of acetic acid (when $HNO_2 = N/4$), this was entirely due to the gradual decom-

* Within the limits of experimental error, the rate of mixing, for instance, which affects the velocity of the reaction, has a decided influence on the above ratios.

position of the former acid.   Urea acetate has been described by Matignon (*Compt. rend.*, 1891, **112**, 1369) as a compound which was completely dissociated in aqueous solution, hence acetic acid could not establish the essential condition required to promote the desired interaction (Expts. IX. and X.).

Decomposition of Urea in the Presence of Two Molecular Proportions of Nitrous Acid.

The results recorded in table I have conclusively proved that urea can be completely decomposed by one molecular proportion of nitrous acid; that this is not accomplished under the conditions which are commonly employed is solely due to the disturbing effect of the secondary reaction (*c*).

Now, according to the usual interpretation of the change, two molecular proportions of nitrous acid should be required to decompose one of urea.

The effect after treating urea directly with nitrous acid in these proportions, and at different concentrations, in the presence of hydrochloric acid to promote the change are given below (for details see Expts. I., II., and III.).

TABLE III.

	Nitrogen evolved. Per cent.	Composition of evolved gases. Per cent.
I. HNO$_2$ N/3, Urea N/6 (2 c.c. N-HCl)	72·02	CO$_2$=35·0, N$_2$=55·4, NO=9·5
II. HNO$_2$ N/6, Urea N/12 (2 c.c. N-HCl)	71·99	CO$_2$=32·1, N$_2$=58·2, NO=9·6
III. HNO$_2$ N/8, Urea N/16 (2 c.c. N-HCl)	69·19	CO$_2$=32·6, N$_2$—57·3, NO=10·0
IV. HNO$_2$ N/10, Urea N/20 (3 c.c. N-HCl)	72·07	CO$_2$=31·1, N$_2$=58·1, NO=10·4

In each case it was readily proved that all the urea had been decomposed, whilst an excess of nitrous acid remained, yet in round numbers only about 70 per cent. of the theoretical proportion of nitrogen was evolved.   The remainder of the nitrogen was, of course, present as ammonium chloride * in the residual solution

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* It is interesting to note that Claus (*Ber.*, 1872, **4**, 140) long ago noticed the formation of ammonia when nitrous acid reacts with urea; thus, he gave the following equation for the reaction in the cold; 2CON$_2$H$_4$+N$_2$O$_3$=

It will be noticed also that, even without allowing for carbon dioxide held in solution, the ratio of carbon dioxide to nitrogen was still well below that of $1:2$ as required.

An equally marked divergence from the theoretical results was obtained by carrying out the reaction in two separate stages. It will be obvious that, according to the usual, but false, explanation of the change, such a procedure should give similar results for each stage. This was not so. Whilst the first stage was represented by the values given under I, table II, the volume of nitrogen evolved in the second stage was equal to only 26·38 per cent. of the original amount of urea present, hence 62·96 + 26·38 = 89·34 per cent.; nitrogen from the remainder of the urea (10·66 per cent.) was fixed as ammonium chloride in the second stage (see Expt. IV.).

The composition of the evolved gases, namely, $CO_2 = 22·4$ per cent., $N_2 = 50·7$ per cent., $NO = 26·8$ per cent., was very different from that of the gases set free in the first stage.

A rather remarkable paradox makes its appearance when the results are compared on the basis of the false and of the true equations; thus, according to the usual interpretation of the reaction, the amount of urea decomposed was roughly 30 per cent. greater (table III) than indicated by the volume of nitrogen set free, whereas in reality the amount of urea decomposed was much less than required by the volume of nitrogen evolved. The paradox, of course, is but a phantom; its existence is just as unreal as the usual explanation of the change is incorrect.

A contemplation of the results just recorded, and so easily demonstrated, makes it almost impossible to believe that the behaviour of urea towards nitrous acid has ever been seriously studied with the object of obtaining evidence to support the supposed "carbamide" formula.*

Whilst the present study of the reaction has supplied further proof of the cyclic formula, it has also brought to light yet another

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$(NH_4)_2CO_3 + 2N_2 + CO_2$. It was assumed, however, that urea was hydrolysed to ammonium carbonate during the process, apparently independent of the reaction with nitrous acid, since the proportion of carbon dioxide to nitrogen evolved is shown to be the same as in the usual equation; probably for this reason, the observation is never mentioned in the text-books.

* Emmerling (A., 1886, **50**, 747; the original paper in *Landw. Versuchs-Stat.*, 1886, 440, was not available) studied the decomposition of urea by nitrous acid in the presence of nitric acid and acetic acid respectively, both in cold and in hot solutions. The volume of nitrogen evolved was found never to be equal to the theoretical, but no apparent attempt was made to offer any explanation of the results.

of the many fallacies which abound throughout the chemistry of urea.

The origin of these is not far to seek.

Instead of a careful study of the properties and reactions of urea being made the groundwork for solving the problem of its constitution, an almost infallible belief in the truth of the carbamide formula has all along been the predominant factor in determining what these properties and reactions should be.

Secondary changes, seemingly unimportant by-products, apparent abnormalities in certain reactions, and so forth, have been pushed aside as of little consequence so long as the end result could be made to fit in with the "carbamide" structure.

EXPERIMENTAL.

With one exception, all the experiments were made with the aid of a Lunge nitrometer. The specimen of sodium nitrite used for the generation of nitrous acid contained 97·18 per cent. of $NaNO_2$;[*] a proportionate weight (71 : 69) corresponding with the theoretical required was used in each case.

Action of Nitrous Acid on Urea in Molecular Proportions of Two to One.

Expt. I.—0·03 Gram of pure urea and 0·071 gram of sodium nitrite dissolved in 1 c.c. of water were introduced into the nitrometer over mercury, and 2 c.c. of N-hydrochloric acid directly added.

Concentration at outset, $HNO_2 = N/3$, $CON_2H_4 = N/6$. The reaction was apparently completed within thirty minutes, whilst more than four-fifths of the gas had been evolved after five minutes. In this and all other experiments not less than one hour was allowed to elapse before the gas was measured and analysed.

Gas evolved = 31·4 c.c. at 18° and 766·5 mm. $CO_2 = 11$ c.c., $NO = 3$ c.c., $N_2 = 17·4$ c.c.

Volume of nitrogen at N.T.P. = 16·134 c.c., = 72·02 per cent. of the theoretical. (Theory = 22·4 c.c. at N.T.P.)

Expt. II.—As above, but $HNO_2 = N/6$, $CON_2H_4 = N/12$.

Gas evolved = 29·7 c.c. at 16° and 763·5 mm. $CO_2 = 9·55$ c.c., $NO = 2·85$ c.c., $N_2 = 17·3$ c.c.

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[*] Estimated by the thiourea method (T., 1912, **101**, 2190, and Coade and Werner, T., 1913, **103**, 1221).

Volume of nitrogen at N.T.P. = 16·126 c.c., = 71·99 per cent. of the theoretical.

Expt. III.—The last experiment was repeated to prove the cause for the deficiency of the evolved nitrogen.

After the evolution of gas had ceased, the residual liquid was well washed out of the nitrometer. It required for neutralisation, using methyl-orange as indicator, 6·1 c.c. of $N/10$-sodium hydroxide. Since 1 c.c. of N-hydrochloric acid was directly neutralised in liberating nitrous acid, there should have remained, according to the usual equation, free acid equivalent to 10 c.c. of $N/10$-sodium hydroxide. Hence $10 - 6·1 = 3·9$ c.c. of $N/10$-hydrochloric acid were neutralised by ammonia from the hydrolysis of cyanic acid. Now, according to equations (*a*) and (*b*) (p. 865), the maximum amount of acid that could be thereby neutralised would be 5 c.c. of $N/10$-hydrochloric acid, therefore 78 per cent. of the theoretical proportion of cyanic acid was hydrolysed, or so much of its nitrogen was fixed as ammonium chloride. The remainder of its nitrogen, namely, 22 per cent., was set free (equation *c*), together with that from urea, in accordance with equation (*a*).

Since all the urea was decomposed with the liberation of half of its nitrogen, we have $50 + 22 = 72$ per cent. of the total nitrogen set free, which was in complete agreement with the result obtained from Expt. II.

As the results with urea and nitrous acid (1 : 2) at lower concentrations (table III) were obtained in a manner similar to the above, further details are unnecessary.

Action of Nitrous Acid on Urea (2 : 1) in Two Stages.

Expt. IV. First Stage.—0·06 Gram of urea and 0·071 gram of sodium nitrite were dissolved in 4 c.c. of water, and 2 c.c. of N-hydrochloric acid directly added.

Concentration, $CON_2H_4 = N/6$, $HNO_2 = N/6$.

Gas evolved = 37·5 c.c. at 18° and 763 mm, $CO_2 = 13·7$ c.c., $NO = 1·6$ c.c., $N_2 = 22·2$ c.c.

Volume of nitrogen at N.T.P. = 20·49 c.c., = 91·46 per cent. of the theoretical.

Second Stage.—The gas having been expelled from the nitrometer (from a repeated experiment), 0·071 gram of sodium nitrite dissolved in 1 c.c. of water was added, and then 1 c.c. of N-hydrochloric acid. The evolution of gas was very much slower than in the first stage, and five hours were allowed for the completion of the reaction.

Gas evolved = 25·3 c.c. at 18° and 769·3 mm. CO_2 = 10·25 c.c., NO = 2·35 c.c., N_2 = 12·7 c.c.

Volume of nitrogen at N.T.P. = 11·82 c.c. = 52·76 per cent. of the theoretical.

An analysis of the residual solution after the first stage showed that 7·15 c.c. of $N/10$-hydrochloric acid had been neutralised, equivalent to 71·5 per cent. of cyanic acid hydrolysed, therefore 28·5 per cent. of the evolved nitrogen was the result of the reaction between nitrous acid and cyanic acid (equation c); hence 91·46 − 28·5 = 62·96 per cent. of the urea present was decomposed in this stage.

Therefore only 37·04 per cent. of urea remained to be attacked by nitrous acid in the second stage, and since 52·76 per cent. of nitrogen was evolved, it follows that 52·76 − 37·04 = 15·72 per cent. of the nitrogen set free in this stage was due to the above reaction (equation c).

A comparison of the results from the two stages is not without interest.

	First stage. Per cent.	Second stage. Per cent.
Urea decomposed	= 62·96	37·04
HNCO hydrolysed	= 71·50	57·60
HNCO decomposed by HNO_2 ...	= 28·50	42·40
Composition of evolved gas...... CO_2 = 36·5		40·5
N_2 = 59·2		50·1
NO = 4·2		9·3
Ratio $CO_2 : N_2$	1 : 1·62	1 : 1·23

Since nitrous acid was in considerable excess in the second stage (which should not be the case, according to the usual equation), the proportion of cyanic acid attacked by it to cyanic acid hydrolysed was much greater than in the first stage.

Decomposition of Urea by One Molecular Proportion of Nitrous Acid.

In order to illustrate how the results given under table I were obtained, it will be sufficient to state the details of the most successful experiment.

Expt. V.—0·12 Gram of urea was dissolved in 3 c.c. of N-hydrochloric acid, and the solution introduced into the nitrometer; 0·071 gram of sodium nitrite dissolved in 2 c.c. of water was placed in the cup (previously rinsed) of the nitrometer, and added gradually in four separate portions to the urea solution. The reaction, which was hastened by shaking to ensure rapid mixing, was allowed to complete itself before each addition of the sodium nitrite.

Gas evolved (after one hour) = 44·2 c.c. at 18° and 766·4 mm.; $CO_2 = 19·6$ c.c.; $NO = 0·6$ c.c.; $N_2 = 24·0$ c.c.

Volume of nitrogen at N.T.P. = 22·252 c.c. = 99·34 per cent. of the theoretical.

The residual solution from a similar experiment required 10·05 c.c. of $N/10$-sodium hydroxide for neutralisation.

Hence 20 (2 c.c. of N-hydrochloric acid originally free) − 10·05 = 9·95 c.c. of $N/10$-hydrochloric acid were neutralised as the result of cyanic acid hydrolysis, which was therefore almost complete. Therefore the amount of urea actually decomposed was 99·34 − 0·5 = 98·84 per cent. of the theoretical, only 0·5 per cent. of the evolved nitrogen being derived from cyanic acid.

Therefore one molecule of urea was decomposed by one molecule of nitrous acid.

Isolation of Cyanic Acid, as the Silver Salt, from the Interaction of Urea and Nitrous Acid.

Expt. VI.—0·6 Gram of urea and 0·71 gram of sodium nitrite were dissolved in 40 c.c. of ice-cold water and to the solution 1·7 grams of silver nitrate previously dissolved in 5 c.c. of water and 5 c.c. of N-nitric acid were added. As the pale cream-coloured precipitate of silver nitrite, which was immediately formed, gradually disappeared, it was replaced by a snow-white precipitate of silver cyanate.

During the progress of the reaction, further 5 c.c. of N-nitric acid were added. After an hour the precipitate was collected, washed, and dried. It gave none of the reactions for nitrous acid, and contained $Ag = 71·84$ per cent. (AgOCN requires $Ag = 72$ per cent.); on adding a few drops of sulphuric acid to the dry salt the characteristic pungent odour of cyanic acid was evolved.

The weight of silver cyanate obtained was 0·63 gram, which was equal to 42 per cent. of the theoretical for equation (d).

The Interaction of Cyanic Acid and Nitrous Acid.

As this change does not appear to have been hitherto examined, the following experiments were made in order to prove the validity of equation (c) already given.

Expt. VII.—0·081 Gram of pure potassium cyanate and 0·071 gram of sodium nitrite were dissolved in 2 c.c. of water and introduced into the nitrometer; 3 c.c. of N-hydrochloric acid were added, that is, 1 c.c. of acid in excess, to counteract the neutralising effects of hydrolysis.

Concentration at outset, HNO_2 and $HNCO = N/5$.

The evolution of gas was very rapid, and the reaction was practically completed within five minutes.

Gas evolved after one hour $= 34.3$ c.c. at $16°$ and 757.8 mm.; $CO_2 = 19.1$ c.c.; $NO = 3.6$ c.c.; $N_2 = 11.6$ c.c.

Volume of nitrogen at N.T.P. $= 10.72$ c.c. $= 47.8$ per cent. of the theoretical. Therefore 52.2 per cent. of cyanic acid had been hydrolysed.

Expt. VIII.—The above experiment was repeated. The residual solution required for neutralisation 8.5 c.c. of $N/10$-sodium hydroxide, instead of 4.78 c.c. as required by the gasometric analysis. The apparent discrepancy was easily explained when the above results were considered. The volume of nitric oxide evolved (3.33 c.c. at N.T.P.) represents a decomposition of 22.3 per cent. of nitrous acid, with the generation of nitric acid equivalent to 0.74 c.c. of $N/10$-sodium hydroxide, whilst the proportion of cyanic hydrolysed showed that free nitrous acid remained equivalent to 3 c.c. of $N/10$-sodium hydroxide. Hence $4.78 + 0.74 + 3.0 = 8.52$ c.c. of $N/10$-sodium hydroxide were required, which is in complete agreement with the value actually found. The presence of unchanged nitrous acid in the residual liquid was easily proved.

Therefore the reaction between cyanic acid and nitrous acid takes place theoretically between equal molecular proportions, but at a concentration of $N/5$ the velocity of hydrolysis of cyanic acid is slightly higher than that of the primary change.

The Behaviour of Urea towards Pure Nitrous Acid alone or in the Presence of Acetic Acid.

Expt. IX.—0.03 Gram of urea and 0.071 gram of sodium nitrite were dissolved in 2 c.c. of water and 2 c.c. of N-acetic acid were added. Concentration of $HNO_2 = N/4$.

There was no preceptible evolution of gas until after a considerable time; thus, after twenty-four hours 7.4 c.c. had been evolved and at the end of ninety-six hours, when the experiment was stopped, the volume of the evolved gas was $= 12.6$ c.c. at $13°$ and 758 mm. The volume of nitrogen at N.T.P. was $= 6.56$ c.c., and the original gas contained 9.5 per cent. of nitric oxide.

The slow action was primarily brought about as a result of the gradual decomposition of nitrous acid, whereby urea nitrate was slowly generated. Râ+y and his co-workers (*loc. cit.*) have shown that even at $0°$ the most concentrated solution of nitrous acid, stable for only a short time, was approximately $N/5.5$.

Expt. X.—The same proportions of urea and sodium nitrite as before were dissolved in 29 c.c. of water, and 1 c.c. of N-acetic acid was added. Concentration of $HNO_2 = N/30$.

After remaining for three days in the nitrometer, the volume of gas evolved was 0·8 c.c. Yet when 2 c.c. of N-hydrochloric acid were added, a fairly brisk reaction was quickly promoted, and even at this low concentration was almost completed at the end of half an hour.

Summary.

(1) Urea is not attacked by pure nitrous acid alone, or even when a second very weak acid is present.

(2) When a salt of urea is produced, by the presence of a sufficiently strong acid, it is immediately attacked by nitrous acid, because an amino-group is thereby presented for such attack.

(3) One molecule of urea (as a salt) requires but one molecule of nitrous acid for its decomposition into nitrogen, cyanic acid, and water, since only one amino-group is present.

(4) Cyanic acid and nitrous acid react in equal molecular proportions, with the production of nitrogen, carbon dioxide, and water.

(5) The usual interpretation of the reaction between urea and nitrous acid, which has been hitherto accepted, is incorrect; first, because it is in contradiction to the experimental facts, and, secondly, because it is based on an erroneous conception of the constitution of urea.

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LXXV.—A Theory of the Mechanism of the Phytochemical Synthesis of certain Alkaloids.

By ROBERT ROBINSON.

ALTHOUGH in recent years, largely owing to the investigations of Pictet and his collaborators, there has been a due recognition of the importance of the rôle played by formaldehyde in the production of alkaloids in plants, and although it is generally admitted (compare Winterstein and Trier, "Die Alkaloide," pp. 263–317) that the amino-acids and carbohydrates are the most probable starting points for the majority of phytochemical syntheses, yet little progress has been made in ascertaining the nature of these processes or even in the less ambitious task of formulating possible mechanisms based on laboratory analogies. The details of the

schemes which have been suggested, with but few exceptions, involve reactions for which little or no parallel exists in synthetical organic chemistry under conditions approximating to those obtaining in a plant. Thus Pictet's view of the mechanism of the synthesis of nicotine was founded on observations of pyrogenic reactions of pyrrole derivatives, and Winterstein and Trier seek to replace this hypothesis by another, according to which the base results from the oxidation of a mixture of pyridine and N-methylpyrrolidine (*loc. cit.*, p. 298). Similar ideas have been advanced by Windaus and Knoop (*Beitr. chem. Physiol. Path.*, 1905, **6**, 392) to explain the formation of xanthine by the oxidation of a mixture of carbamide and methylglyoxaline and of histidine by an analogous process applied to glycine and methylglyoxaline.

There has thus been a tendency to explain the results observed by the assumption that plants have at their command enormously powerful reagents that are able to cause substances, the properties of which have been investigated with considerable care, to undergo transformations which cannot be induced in the laboratory. To a certain extent, and especially in regard to oxidation and reduction, this must be true, but it is probable that this aspect has been exaggerated and that an equally important cause of the variety and complexity of syntheses in plants resides in the highly reactive nature of the substances which function as intermediate products.

The point of view reached in the present communication is due to a development of ideas which owed their inception to the hypothesis that the synthesis of tropinone recently described (this vol., p. 762), on account of its simplicity, is probably the method employed by the plant, and confirmation of this theory was sought and found in the structures of hygrine and cuschygrine, which stand to one another in the same relation as styryl methyl ketone (benzylideneacetone) to distyryl ketone (dibenzylideneacetone). Having found it desirable to proceed from ornithine in order to reach the bases of the pyrrolidine group, it was obviously interesting to inquire as to whether similar methods applied to the homologous lysine would lead to naturally occurring piperidine compounds. This proved to be the case, and the investigation was then extended to include the more important of the alkaloids the constitutions of which have been determined. In the schemes given in the sequel, linking of carbon to carbon is traced to two processes only, namely, the aldol condensation and the very similar condensation of carbinol-amines, resulting from the combination of an aldehyde or ketone and ammonia or an amine, and containing the group ·$\overset{\cdot}{C}$(OH)·$\overset{\cdot}{N}$·, with substances containing the group ·$\overset{\cdot}{C}$H·CO·.

The latter reaction has been investigated chiefly in connexion

with cotarnine and similar pseudo-bases, and the production of anhydrocotarnineacetone (I) may be cited as a typical example:

$$\begin{matrix} C_8H_6O_3\text{---}CH\cdot OH \\ | \\ CH_2\cdot CH_2\cdot NMe \end{matrix} + CH_3\cdot CO\cdot CH_3 \longrightarrow \begin{matrix} C_8H_6O_3\text{---}CH\cdot CH_2\cdot CO\cdot CH_3 \\ | \\ CH_2\cdot CH_2\cdot NMe \end{matrix}$$
$$(I.)$$
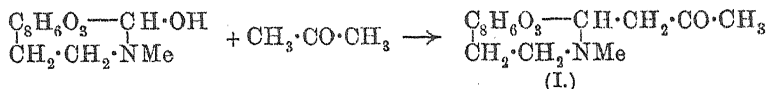
The condensing agent employed by Liebermann and Kropf (*Ber.*, 1904, **37**, 211) in this case is unnecessary, and the reaction proceeds to completion in aqueous solution and at the ordinary temperature. In fact, these pseudo-bases are substances which enter into a variety of condensations with the greatest facility, and a large number of substances have been prepared in this way, and in most cases in good yield.

Employing these admissible methods it is possible in each instance to obtain the alkaloid skeleton, and the further modifications are usually made by means of oxidations or reductions and by elimination of water with the formation of an aromatic nucleus or occasionally of an ethylene derivative. The more important starting points employed are ammonia and formaldehyde, ornithine (arginine) and lysine and degradation products of carbohydrates. Of the latter, citric acid is suggested as the source of acetone residues which it supplies in the form of acetonedicarboxylic acid as the result of oxidation. Seekamp has observed the formation of acetone (*Annalen*, 1893, **278**, 374) by the photochemical decomposition of a 5 per cent. aqueous solution of citric acid containing 1 per cent. of uranium oxide, and it can scarcely be doubted that the dicarboxylic acid was an intermediate product. The author does not, however, wish to emphasise unduly this theory of the source of the acetone residues, and it is interesting to note that Lippmann (*Ber.*, 1893, **26**, 3057) found that acetonedicarboxylic acid was obtained during the spontaneous decomposition of calcium trisaccharate. Further, a reactive acetone derivative may be found in diacetylacetone or other 'polyketen,' the formation of which in plants has been discussed by Collie (*T.*, 1893, **63**, 329; 1907, **91**, 1806), and in that case the acetyl groups would be removed by hydrolysis subsequent to the condensations. However, the occurrence of the carboxyl group in ecgonine suggests that in the synthesis of cocaine it is a carboxylated acetone derivative which is the forerunner of the alkaloid. Except in the cases of hygrine and tropinone, the carboxyl groups have been omitted from the acetone rests for the sake of simplicity in representation. As a starting point for both quinoline and *iso*quinoline bases, it has been found convenient to assume the intervention of acetylglycollaldehyde (II), or Δ^α-butene-$\alpha\beta$-diol-γ-one, a substance which has not yet been isolated. It may readily be derived from a pentose or

methylpentose by loss of water and oxidation, as shown below, and it is perhaps significant that a methylpentose, quinovose, occurs in a state of combination as quinovin in cinchona-bark.

$$OH \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CHO$$

$$CH_3 \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CHO$$

$$-H_2O \qquad \downarrow \text{Oxidation}$$

$$CH_3 \cdot CO \cdot CH(OH) \cdot CH(OH) \cdot CHO$$

$$\downarrow \text{Oxidation}$$

$$CH_3 \cdot CO \cdot CH(OH) \cdot CHO \rightleftharpoons CH_3 \cdot CO \cdot C(OH) : CH \cdot OH$$

$$(II.)$$
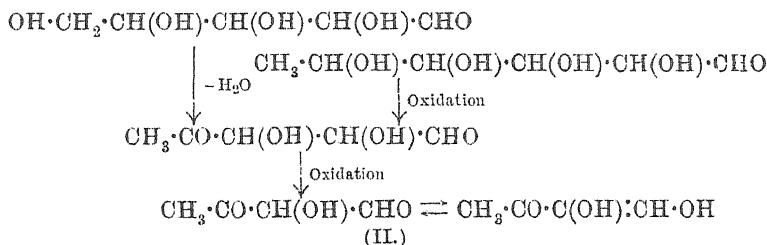
The Pyrrolidine Group.

It has recently been demonstrated by Hess (*Ber.*, 1913, **46**, 4104 [*]) that the methylation of an amine with the aid of formaldehyde is accompanied by oxidation, amino-alcohols yielding methylaminoketones. The methylating and oxidising action of formaldehyde on ornithine might therefore yield a carbinol-amine of the pyrrolidine series in accordance with the equation

$$NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H + CH_2O =$$

$$NHMe \cdot CH_2 \cdot CH_2 \cdot CHO \left[\rightarrow \begin{array}{c} CH_2 \cdot CH(OH) \\ CH_2 \longrightarrow CH_2 \end{array} {>}NMe \right] + NH_3 + CO_2.$$
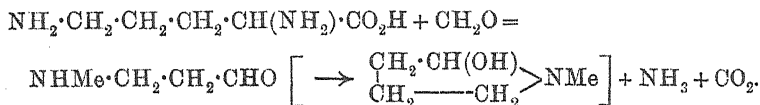
Naturally, the possibility is not excluded that the oxidation of the amino-acid [†] is preceded by the formation of a hydroxy-acid, and ammonia and alcohols may in all cases be intermediate between amines and the aldehydes obtained by oxidation.

Further oxidation accompanying methylation might attack both

[*] In which a complete list of references to earlier work by Eschweiler and others will be found.

[†] Dakin (*J. Biol. Chem.*, 1906, **1**, 171) has applied Fenton's method of oxidation by means of hydrogen peroxide and a trace of ferrous sulphate to the ammonium salts of the amino-acids, and has obtained aldehydes, ammonia, and carbon dioxide. Hurtley and Wootton (T., 1911, **99**, 288) find that alloxan effects the same change which had already been observed in the particular instances of the conversion of alanine into acetaldehyde and of leucine into *iso*valeraldehyde by Strecker (*Annalen*, 1862, **123**, 363).

Quite recently Schweitzer (*Biochem. Zeitsch.*, 1916, **78**, 37) has shown that the tyrosinase from potatoes can oxidise glycine with the formation of formaldehyde, carbon dioxide, and ammonia. The reaction takes place in the presence of an alkali, preferably calcium hydroxide, and appears to be accelerated by chlorophyll.

ends of the molecule, with the production of succindialdehyde * and methylamine, as shown below :

$$NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H + 2CH_2O =$$

$$CHO \cdot CH_2 \cdot CH_2 \cdot CHO \left[\ \rightarrow \ \begin{matrix} CH_2 \cdot CH(OH) \\ CH_2 \cdot CH(OH) \end{matrix} \Big> NMe \right] + 2NH_3Me + CO_2.$$
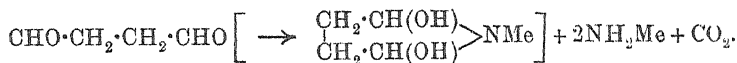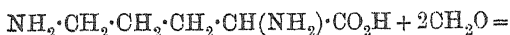
After condensation with acetonedicarboxylic acid and elimination of carbon dioxide, hygrine (III), cuschygrine (IV), and tropinone (V) are obtained. The synthesis of the latter base (this vol., p. 762) by means of the reaction here assumed to occur in nature was accomplished in dilute aqueous solution at the ordinary temperature. Willstätter (*Ber.*, 1900, **33**, 1161) has already given reasons for supposing that the synthesis of atropine and its congeners and of cocaine is preceded by that of tropinone, and it is now possible to add that the carboxyl of cocaine † is the result of partial decomposition of tropinonedicarboxylic acid, possibly occasioned by the formation of the methyl ester or of an acid salt. In the latter case, the process resembles that which Bandrowski employed for the preparation of propiolic acid from acetylenedicarboxylic acid (*Ber.*, 1880, **13**, 2340). The question of the synthesis of benzoic and tropic acids is not examined here, since there is no evidence from accompanying hydroaromatic compounds as to how these may be derived from the carbohydrates.

* Succindialdehyde would be more readily obtained from a diaminoadipic acid which does not, however, appear to have been isolated.

† The simplest substance produced on the cocaine model is probably arecoline, a comparison of the formula of which with that of cocaine shows that the only divergences, which it is necessary to postulate in the synthesis of the former from that of the latter, are the employment of two molecules of formaldehyde instead of one of succindialdehyde and loss of water instead of benzoylation.

Cocaine.   Arecoline.   Trigonelline.
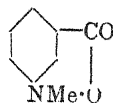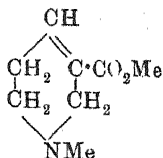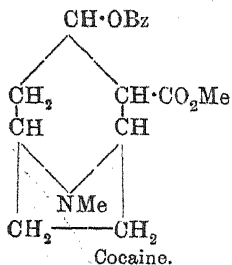
Arecoline also closely resembles a hypothetical intermediate in the synthesis of nicotine. If it is oxidised, as was assumed for that more complex tetrahydropyridine, then the betaine trigonelline would be obtained.

$$\begin{array}{c} NMe \\ \diagup \backslash \\ CH_2 \quad CH \cdot OH \\ CH_2\text{---}CH_2 \end{array} \qquad \begin{array}{c} CO_2H \\ CH_2 \cdot CO \cdot CH_2 \cdot CO_2H \end{array} \longrightarrow$$

$$\begin{array}{c} NMe \\ \diagup \backslash \quad CO_2H \\ CH_2 \quad CH \cdot CH \cdot CO \cdot CH_2 \cdot CO_2H \\ CH_2\text{---}CH_2 \end{array} \longrightarrow \begin{array}{c} NMe \\ \diagup \backslash \\ CH_2 \quad CH \; CH_2 \cdot COMe \\ CH_2\text{---}CH_2 \end{array}$$

(VI.)   (III.)

$$\begin{array}{c} NMe \\ \diagup \backslash \\ CH_2 \quad CH \cdot OH \\ CH_2\text{---}CH_2 \end{array} \quad \begin{array}{c} CO_2H \quad CO_2H \\ CH_2 \cdot CO \cdot CH_2 \end{array} \quad \begin{array}{c} NMe \\ \diagup \backslash \\ HO \cdot CH \quad CH_2 \\ CH_2\text{---}CH_2 \end{array} \longrightarrow$$

$$\begin{array}{c} NMe \\ \diagup \backslash \\ CH_2 \quad CH \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH \quad CH_2 \\ CH_2\text{---}CH_2 \qquad\qquad CH_2\text{---}CH_2 \end{array} + 2CO_2 + 2H_2O$$

(IV.)

$$\begin{array}{c} CH \cdot OH \quad CH_2 \cdot CO_2H \\ CH_2 \\ \quad NMe \quad CO \\ CH_2 \\ CH \cdot OH \quad CH_2 \cdot CO_2H \end{array} \longrightarrow \begin{array}{c} CH\text{---}CH \cdot CO_2H \\ CH_2 \\ \quad NMe \; CO \\ CH_2 \\ CH\text{---}CH \cdot CO_2H \end{array} \longrightarrow \begin{array}{c} CH\text{---}CH_2 \\ CH_2 \\ \quad NMe \; CO \\ CH_2 \\ CH\text{---}CH_2 \end{array}$$

(V.)

Ecgonine

↓

Benzoyl ecgonine   Reduction

↓

Cocaine

$$\begin{array}{c} CH\text{---}CH \cdot CO_2K(Me) \\ CH_2 \\ \quad NMe \; CO \\ CH_2 \\ CH\text{---}CH_2 \end{array}$$

Reduction

Tropine ψ-Tropine

↓   ↓

Hyoscyamine, Tropa-
atropine, etc. cocaine.

The condensation product (VI), which forms the source of hygrine, may also be the progenitor of nicotine (VIII), and the reactions necessary involve condensation with formaldehyde and ammonia to a piperidone (VII) containing the nicotine skeleton, after which there are alternative ways of expressing the remaining stages.

M M *

$$CO \quad CO_2H \quad NMe$$

$$CO_2H \cdot CH_2 \quad CH \text{———} CH \quad CH_2 \longrightarrow$$
$$CH_2O \quad CH_2O \quad CH_2 \text{—} CH_2$$
$$NH_3$$

(VI.)

$$CO \qquad NMe \qquad\qquad CH \cdot OH$$

$$CH_2 \quad CH \text{——} CH \quad CH_2 \quad \xrightarrow{\text{Reduction}} \quad CH_2 \quad CH-$$
$$CH_2 \quad CH_2 \quad CH_2\text{-}CH_2$$
$$NH$$

(VII.)

$$\bigg| -H_2O$$

$$NMe \qquad\qquad CH$$

$$\text{—}CH \quad CH \qquad \xleftarrow{\text{Oxida-tion}} \quad CH_2 \quad C\text{——}$$
$$CH_2\text{--}CH_2$$
$$N$$

(VIII.)
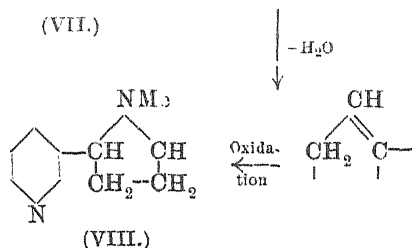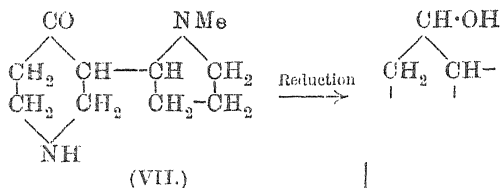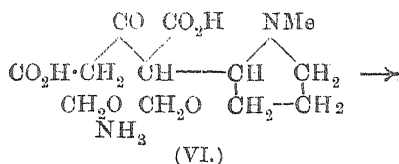
The Piperidine Group.

Starting from lysine * (IX) and proceeding as illustrated above in the case of the lower homologue ornithine, the formation of the bases X and XI would be anticipated. The latter is the alkaloid ψ-pelletierine, isolated by Ciamician and Silber and by Piccinini from the root-bark of the pomegranate tree, and since tropinone has not yet been obtained from natural sources, the occurrence of its ring homologue is particularly valuable evidence. The base X has been synthesised by Hess, Merck, and Uibrig (*Ber.*, 1915, **48**, 1886), and later identified by Hess and Eichel (*Ber.*, 1917, **50**, 380) with a methylpelletierine occurring in small relative amount in the alkaloids of the pomegranate tree.

$$NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$$
(IX.)

$$CH_2$$
$$CH_2 \quad CH_2$$
$$CH_2 \quad CH \cdot CH_2 \cdot COMe$$
$$NMe$$

(X.)

$$CH_2\text{—}CH\text{——}CH_2$$
$$CH_2 \quad NMe \quad CO$$
$$CH_2\text{—}CH\text{——}CH_2$$
(XI.)
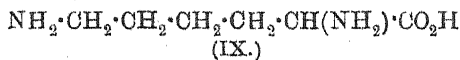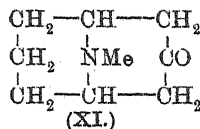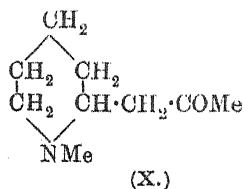
* Clearly the source through cadaverine of the piperidine rest which appears in piperine.

The frequent concurrence of closely related alkaloids, such as the pelletierines * or coniine and its associates, is probably to be explained by variations of some primary product due to alternate hydration and dehydration or by oxidation and reduction.   In this connexion, a highly significant discovery has been reported by Hess, Eichel, and Uibrig (*Ber.*, 1917, **50**, 351), who find that the reaction between amino-alcohols and formaldehyde is reversible. The methylaminoketone (X), for example, is decomposed in alcoholic solution by semicarbazide acetate, with the formation of the demethylated amino-alcohol (XII) and formaldehydesemi-

$$
\begin{array}{ccc}
& \text{CH}_2 & \text{CH}_2 \\
\text{(X)} \;\rightarrow\; \substack{\text{CH}_2 \;\; \text{CH}_2 \\ \text{CH}_2 \;\; \text{CH·CH}_2\text{CH(OH)·CH}_3 \\ \text{NH}} & \longrightarrow & \substack{\text{CH}_2 \;\; \text{CH}_2 \\ \text{CH}_2 \;\; \text{CH·CH}_2\text{·CH}_2\text{·CH}_2 \\ \text{NH}} \\
& \text{(XII.)} & \text{(XIII.)}
\end{array}
$$

$$
\substack{\text{CH}_2 \\ \text{CH}_2 \;\; \text{CH}_2 \\ \text{CH}_2 \;\; \text{CH·CH}_2\text{·CH}_2\text{·CH}_3 \\ \text{NMe}}
$$
(XIV.)

$$
\substack{\text{CH}_2 \\ \text{CH}_2 \;\; \text{CH}_2 \\ \text{CH}_2 \;\; \text{CH·CH:CH·CH}_3 \\ \text{NH}} \;\longrightarrow\; \substack{\text{CH}_2 \\ \text{CH}_2 \;\; \text{CH}_2 \\ \text{CH}_2 \;\; \text{CH·CH(OH)·CH}_2\text{·CH}_3 \\ \text{NH}} \;\longrightarrow
$$
(XV.)

$$
\substack{\text{CH}_2 \\ \text{CH}_2 \;\; \text{CH}_2 \\ \text{CH}_2 \;\; \text{C:CH·CH}_2\text{·CH}_3 \\ \text{NH}} \;\longrightarrow\; \substack{\text{CH}_2 \\ \text{CH}_2 \;\; \text{CH} \\ \text{CH}_2 \;\; \text{C·CH}_2\text{·CH}_2\text{·CH}_3 \\ \text{NH}}
$$
(XVI.)
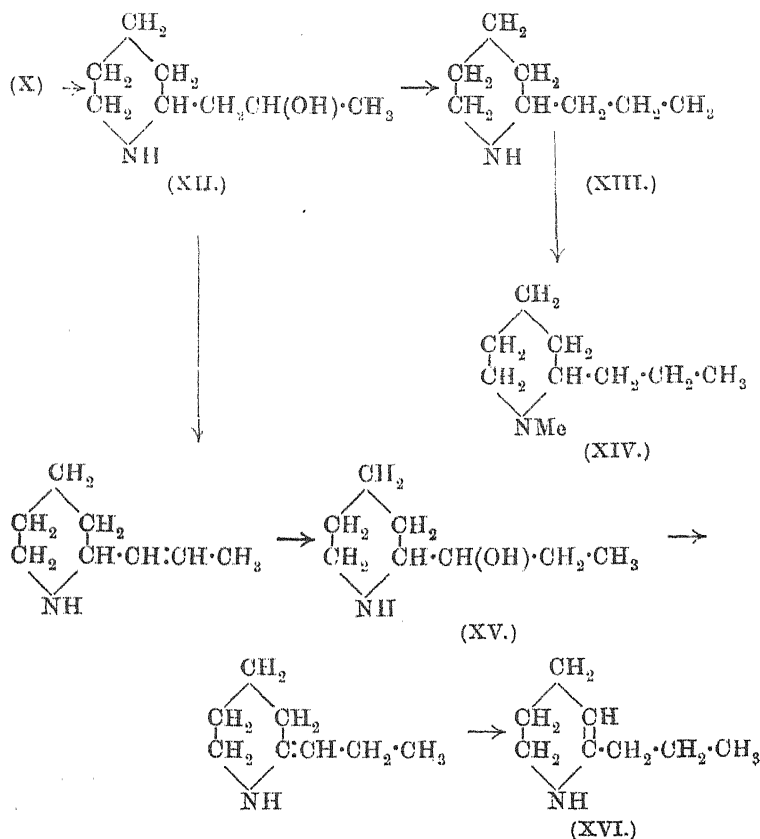
* The imino-ketone pelletierine, containing one reactive methylene-group (Hess and Eichel, *loc. cit.*), has not yet been completely investigated, but, on the evidence so far recorded, and from analogy it should be the ketone corresponding with conhydrine or, more probably, the 3-piperidone obtained by addition of water to coniceine followed by oxidation.   In either case it will fit into the lysine-acetone scheme.

carbazone. This suggests not only that oxidation accompanies
N-methylation and O-methylation, but also that reduction is
associated with N-demethylation. Coniine (XIII), N-methyl-
coniine (XIV), conhydrine (XV), and coniceine (XVI) represent
on this view modifications of the amino-alcohol (XII), and therefore
of the normal product (X), from lysine, formaldehyde, and a
reactive acetone derivative.

In the above, and also in some of the sections which follow, the
reduction of alkylamines has been assumed, and it may be pointed
out that there is evidence that these substances are reducible, the
reaction probably depending on the intermediate formation of an
unsaturated or cyclic ammonium hydroxide.

The Quinuclidine Group.

Condensations between formaldehyde, ammonia, and a reactive
acetone derivative, such as acetonedicarboxylic acid, can explain
in an astonishingly simple manner the formation of alkaloids con-
taining the curious quinuclidine ring system. Ammonia, three
molecules of formaldehyde, and the acetone derivative lead to the
formation of the piperidone (XVII), two molecules of which enter
another molecule of acetone derivative, producing XVIII. This,
owing to the stability of the ring system produced, undergoes
internal aldol condensation, and complete reduction then results in
sparteine (XIX).

$$
\begin{array}{c}
\text{CH}_2\ \overset{\overset{\displaystyle\text{OH}}{|}}{\text{CH}_2}\diagdown\text{CH}\cdot\text{CH}_2\cdot\text{CH}\ \ \overset{\overset{\displaystyle\text{OH}}{|}}{\text{CH}_3}\ \ \text{CH}_2 \\
\text{CH}_2\ \ \text{CH}_2\ \ \text{CH}_2\qquad \text{CH}_2\ \ \text{CH}_2\ \ \text{CH}_2 \\
\diagdown\ \text{N}\ \diagup \qquad\qquad \diagdown\text{N}\diagup
\end{array}
$$

(XIX.)

$$
\begin{array}{c}
\text{CH}_2\ \overset{\overset{\displaystyle\text{C}\cdot\text{OH}}{|}}{\text{CH}_2}\diagdown\text{CH}\cdot\text{CO}\cdot\text{CH}\ \ \overset{\overset{\displaystyle\text{C}\cdot\text{OH}}{|}}{\text{CH}_2}\diagdown\text{CH}_2 \\
\text{CH}_2\ \ \text{CH}_2\ \ \text{CH}_2\qquad \text{CH}_2\ \ \text{CH}_2\ \ \text{CH}_2 \\
\diagdown\text{N}\diagup \qquad\qquad \diagdown\text{N}\diagup
\end{array}
$$
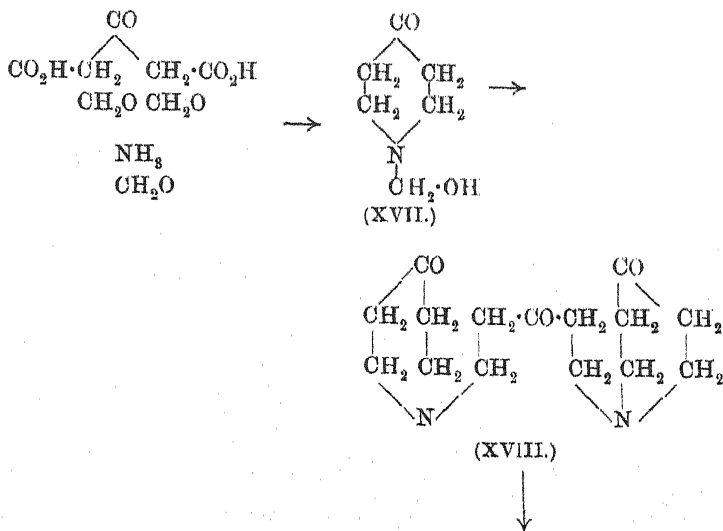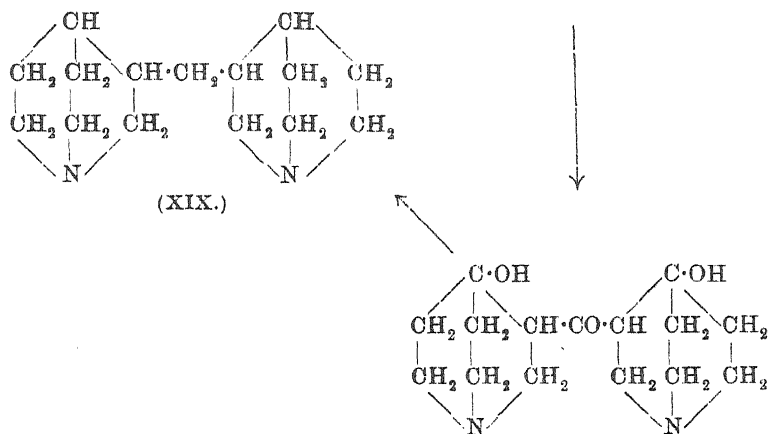
Sparteine thus appears as the reduction product of a substance obtained by condensation along normal lines of three molecules of an acetone derivative with six of formaldehyde and two of ammonia. In the presence of an excess of the acetone derivative, or with such a substance containing only one highly reactive methylene group, for example, acetoacetic acid, the reaction with formaldehyde and ammonia might take a different course, resulting in the formation of the diketone (XX), and this is believed to be

(XX.)

$$
\begin{array}{c}
\overset{\displaystyle\text{CO}}{\diagup} \\
\text{CH}_3\ \text{CH}_2\ \ \text{CH}_2\cdot\text{CO}\cdot\text{CH}_3 \\
\text{CH(OH)}\cdot\text{CHO}\ \ \text{CH}_2\ \ \text{CH}_2 \\
\text{NH}
\end{array}
$$

[MeO]

(XXI.)

$$
\begin{array}{c}
\overset{\displaystyle\text{CO}}{\diagup} \\
\text{CH}_2\ \text{CH}_2\ \ \text{CH}_2\cdot\text{CO}\cdot\text{CH}_3 \\
\text{CH(OH)}\cdot\text{CH}\ \ \text{CH}_2\ \ \text{CH}_2 \\
\text{N}
\end{array}
$$

[MeO]

(XXII.)

CH

CH₂ CH₂ CH·CH(OH)·CH₃

CH(OH)·CH   CH₂   CH₂

[MeO]

N

Aldol condensation

Reduction

C·OH

CH₂   CH₂   CH·CO·CH₃

CH(OH)·CH   CH₂   CH₂

[MeO]

N

- H₂O

CH

CH₂   CH₂   CH·CH:CH₂

CH(OH)·CH   CH₂   CH₂

[MeO]

N

CO   CO·CH₃

CH₂   CH₂   CH₂   Reduction

φ·CH(OH)·CH   CH₂   CH₂

N

(XXII.

C(OH)·C(OH)·CH₃

CH₂   CH₂   CH₂

φ–CH(OH)·CH   CH₂   CH₂

N

Reduction

- H₂O

CH—C(OH)·CH₃

CH₂   CH₂   CH₂

φ–CH(OH)·CH   CH₂   CH₂

N

or

C(OH)·CH·CH₃

CH₂   CH₂   CH₂

φ–CH(OH)·CH   CH₂   CH₂

N

the origin of cinchonine and quinine. The quinoline derivative (XXI) enters the molecule in the manner assumed throughout, that is, by a carbinol-amine condensation, and the remainder of the reactions are of the type already formulated in the case of sparteine. An alternative for the later stages is presented in the scheme which is given below. It is possible that reduction of the diketone (XXII) produces, first, an internal pinacone (compare Kipping and Perkin, T., 1891, **59**, 214), which, after further reduction, undergoes a transformation of the ring system accompanied by elimination of water.

With regard to the genesis of the quinoline derivatives required for cinchonine and quinine, it is natural to seek an explanation from the constitution of quinic acid (XXIII), which accompanies these alkaloids in the plant and is readily converted into quinol derivatives. The coincidence that quinine is also, in a sense, a derivative of p-aminophenol strengthens the conviction that quinic acid is the source of the quinoline half of the molecule. In any case, it would seem necessary that the acid should become oxidised to the ketone (XXIV), so as to provide the six-carbon system and admit the entry of the nitrogen atom. Further, a reactive

CH(OH)·CHO   CH(OH)·CHO

CH   C   CH   C

CH·OH   C   CH   HO·CH$_2$·OCH   C   CH
                          $+CH_2O$
CH   C   CH$_2$ $\xrightarrow{}$ CH   C   CH$_2$

CH   N   CH   N

$\downarrow$ $-H_2O$ $\downarrow$ $-H_2O$

CH(OH)·CHO   CH(OH)·CHO

MeO

N   N
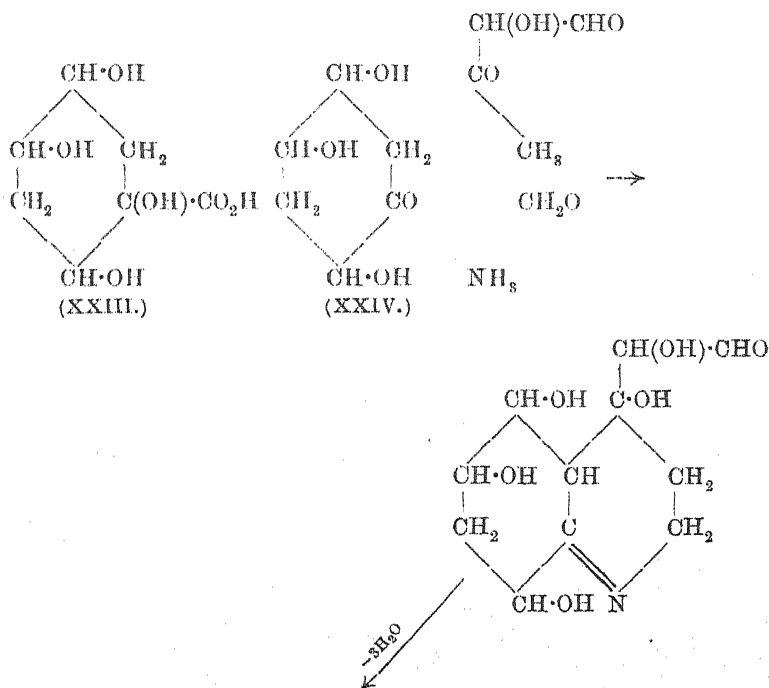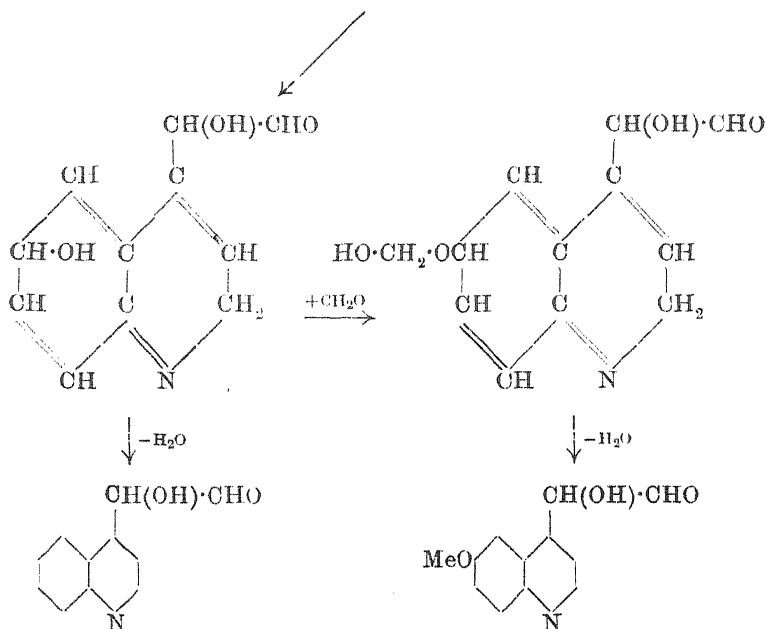
methylene group is so produced, enabling the occurrence of the condensation which closes the quinoline ring. This process is formulated below, and the heterocyclic nucleus is obtained by a reaction similar to that by means of which quinaldine may be synthesised from *o*-aminobenzaldehyde and acetone.

In the majority of the complex examples discussed, it is obvious that the order in which the reactions may be supposed to occur can be considerably varied without fundamentally altering the character of the suggested processes, and in the case of quinine there are several plausible variations of this kind, the most important of which is perhaps that the quinoline ring may be closed immediately after the appearance of an acetyl group in a modified carbohydrate, such as quinovose, and the product must then suffer further degradation by oxidation of the side-chain.

The iso*Quinoline Group.*

In the discussion of this large and important group, it will clear the ground to construct, in the first place, a table which it is considered represents the genetic relationships of the more important members.

Carbohydrate degradation products + ammonia
↓
Hydroaromatic base (HB) ⟶ Hydroaromatic aldehyde (HA)
↓   ↓
Aromatic base (AB)   ⟶   Aromatic aldehyde (AA)

$(HB + HA - H_2O)$

Reduction ╱   │ Oxidation   ╲
╱   ↓   ╲
Morphine   Bulbocapnine   *iso*Thebaine
Codeine   Corytuberine, etc.
↓Thebaine

$(HB + AA - H_2O)$
↓
Glaucine, dicentrine

$(AB + AA - H_2O)$
↓
Norcorydaline ⟵ Norlaudanosine ⟶ Laudanine,   laudanosine,
│   │   papaverine,   xanthaline,
↓   ↓   hydrastine
Corydaline   Norcanadine
↓
Canadine, berberine, protopine, cryptopine.

$(HB + CH_2O)$ ⟶ Pyrogallol derivative $+ AA - H_2O$
↓
Narcotine, narceine.

[?(AB + HA) ⟶ Hydrastine, norcanadine, etc., corydaline.]

A. *The Hydroaromatic base* (XXV) *and Aldehyde* (XXVI).—
The clue to the nature of the hydroaromatic substances from which
the *iso*quinoline bases are derived is given by the constitution of
morphine, and it is regrettable that general agreement on this
subject has not yet been reached.   However, it is only the
"Pschorr formula" which it has been found possible to dissect
in such a manner as to show a relation with the other opium
alkaloids, and this formula has been adopted especially since the
formulæ which it is suggested should replace it cannot without
hesitation be accepted as superior expressions of the properties of
the substance.   By working back from morphine, a scheme for
the synthesis of the *iso*quinoline alkaloids by means of aldol con-
densations has been deduced, and the preliminary stages, starting

from ammonia, formaldehyde,* a reactive acetone derivative, and acetylglycollaldehyde, are represented below.

$$CH_3 \cdot CO \cdot CH(OH) \cdot CHO + CO_2H \cdot CO \cdot CH_2 \cdot CO \cdot CO_2H$$

$$\downarrow$$

$$CH_3 \cdot CO \cdot CH(OH) \cdot CH(OH) \cdot CH_2 \cdot CO \cdot CH_3 + CH_2O + NH_3$$

$$\downarrow$$

$$
\begin{array}{c}
CO \\
HO \cdot CH \quad CH_3 \\
HO \cdot CH \quad CO \cdot CH_2 \cdot CH_2 \cdot NH_2 \\
CH_2
\end{array}
$$

$$\xrightarrow[\text{condensation}]{\text{Aldol}}$$

$$
\begin{array}{c}
CO \\
HO \cdot CH \quad CH_2 \\
HO \cdot CH \quad C(OH) \cdot CH_2 \cdot CH_2 \cdot NH_2 \\
CH_2 \\
(XXV) \ (HB)
\end{array}
$$

$$\downarrow -H_2O$$

$$
\begin{array}{c}
CO \\
HO \cdot CH \quad CH \\
CH \quad C \cdot CH_2 \cdot CH_2 \cdot NH_2 \\
CH
\end{array}
$$

Oxidation $\longleftarrow$

$$
\begin{array}{c}
CO \\
HO \cdot CH \quad CH_2 \\
HO \cdot CH \quad C(OH) \cdot CH_2 \cdot CHO \\
CH_2 \\
(XXVI.) \ (HA)
\end{array}
$$

$$\downarrow -H_2O$$

$$
\begin{array}{c}
OH \\
HO \diagup \diagdown \\
\diagdown \diagup CH_2 \cdot CHO \\
(XXVIII.) \ (AA)
\end{array}
$$

$$\downarrow$$

$$
\begin{array}{c}
OH \\
HO \diagup \diagdown \\
\diagdown \diagup CH_2 \cdot CH_2 \cdot NH_2 \\
(XXVII.) \ (AB)
\end{array}
$$
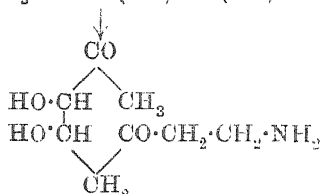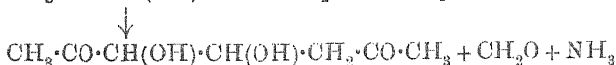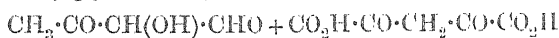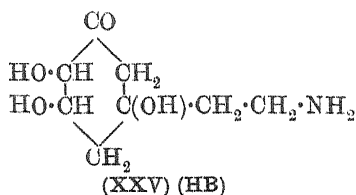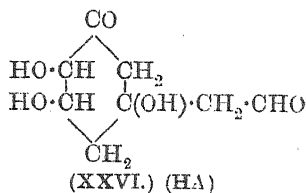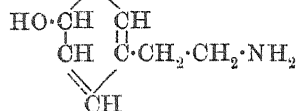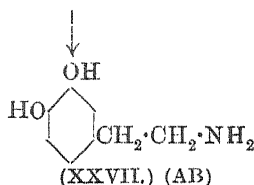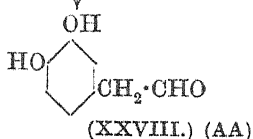
* In all cases where formaldehyde is supposed to enter into a carbinol-amine condensation it is clearly equivalent to assume the intervention of glyoxylic acid or even of an aldehyde, R·CHO, in which the group R is readily oxidisable to carboxyl after the condensation.

(a) $\cdot CO \cdot CH_3 + CH_2O + NH_3 \longrightarrow \cdot CO \cdot CH_2 \cdot CH_2 \cdot NH_2.$

(b) $\cdot CO \cdot CH_3 + CHO \cdot CO_2H + NH_3 \longrightarrow \cdot CO \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H.$

(c) $\cdot CO \cdot CH_3 + CHO \cdot CH_2 \cdot OH \ (e.g.) \ + NH_3 \longrightarrow$
     $\cdot CO \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot OH$
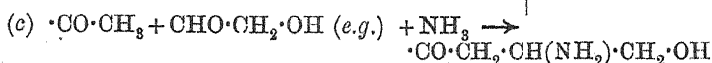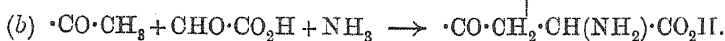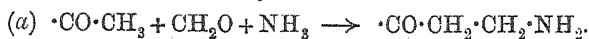
The amino-acids formed in such reactions must be α-amino-acids, and the elimination of carbon dioxide will therefore always be explicable. The

B. *Formation of the Aromatic Compounds.*—Simple dehydration of XXV and XXVI leads to 3:4-dihydroxyphenylethylamine (XXVII) and 3:4-dihydroxyphenylacetaldehyde (XXVIII), and attention is directed to the peculiarity of the constitution of the hydroaromatic substances, which renders it extremely improbable that an orientation in the benzene derivatives other than that observed could result from the process. Oxidation of XXV would, however, produce a pyrogallol derivative, and this oxidation might be the result of methylenation of the two adjacent hydroxyl groups preventing the removal of oxygen from the ring. The dihydrobenzene so obtained would then be oxidised to XXIX.
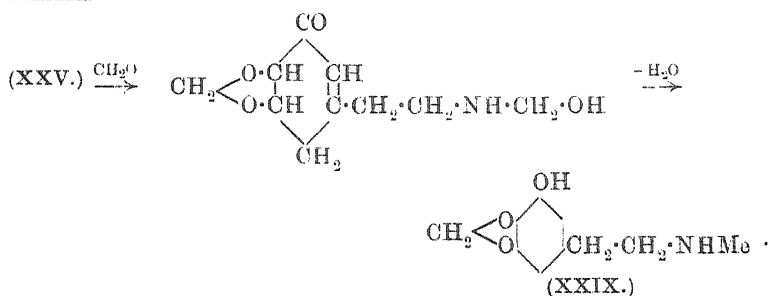
C. *Elaboration of the Morphine Sub-group.*—The hydroaromatic aldehyde (XXVI) condenses with the hydroaromatic base (XXV), producing XXX, XXXI, and XXXII by a carbinol-amine condensation, an internal aldol condensation, and by elimination of water. At this stage, in order to obtain morphine it is necessary to assume the only reduction which is encountered in the whole group. The hydroxyl group marked (*a*) is in a position with respect to the nitrogen atom which renders plausible

syntheses of histidine, tryptophane, and tyrosine probably involve reactions of this type. In the case of histidine the complete representation would be the following:
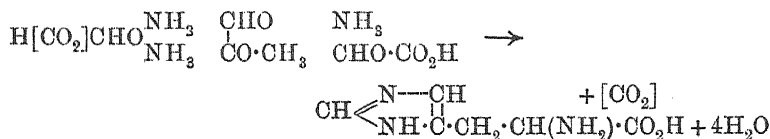
In general, the group ·CO·CH$_3$ becomes ·CO·CH$_2$·CH(NH$_2$)·CO$_2$H, and the carbonyl group can then take part in aldol condensations leading to cyclic structures, whilst the carboxyl group may be eliminated or the amino-acid be oxidised to an aldehyde. The adoption of such a view in the case of the forerunner of the *iso*quinoline alkaloids is favoured by the author, but the simpler suggestion is retained in the text in order to avoid undue complexity of the formulæ.

CH·OH

CO   CH·OH   (XXVI.)
CH₂   CH₂

C·OH

CH₂

CO   CHO
HO·CH CH₂   NH₂
HO·CH C·OH CH₂

CH₂ CH₂
(XXV.)

$\xrightarrow{\text{Carbinol-amine condensation}}$

CH·OH

HO·CH   CH₂
CO   C·OH

CH₂ CH₂
CO   CH
HO·CH CH   NH
HO·CH C·OH CH₂

CH₂ CH₂
(XXX.)

$\downarrow$ Aldol condensation

CH·OH

HO·CH   CH₂
CO   C·OH

CH   CH₂
C·OH CH
HO·CH CH   NH
HO·CH C·OH CH₂

CH₂ CH₂
(XXXI.)

$\xleftarrow{-2\text{H}_2\text{O}}$

HO
HO

CH₂
C·OH CH
HO·CH CH   NH
HO·CH C·OH(a) CH₂

CH₂ CH₂
(XXXII.)

$\downarrow$ Reduction N-methylation

HO
HO

CH₂
C·OH CH
HO·CH CH   NMe
HO·CH CH   CH₂

CH₂ CH₂

$\xrightarrow{-2\text{H}_2\text{O}}$

HO

CH₂
O   C   CH
OH   C   NMe
HO·CH CH   CH₂

CH₂ CH₂
(XXXIII.)

the assumption of the formation of a cyclic ammonium hydroxide and after the reduction morphine (XXXIII) is obtained by *N*-methylation and elimination of two molecules of water. *O*-Methylation, in addition, provides codeine, and thebaine is the result of still further methylation, accompanied by loss of two atoms of hydrogen.

D. *The Aromatic Phenanthrene Sub-group.*—The compound XXXII, by symmetrical elimination of three molecules of water, yields the phenol derivative (XXXIV), which by *N*-methylation and methylation of two phenolic hydroxyl groups becomes *isothebaine* (XXXV), which Klee (*Arch. Pharm.*, 1914, **252**, 211) has shown accompanies thebaine in *Papaver orientale.*

(XXXIV.)   (XXXV.)
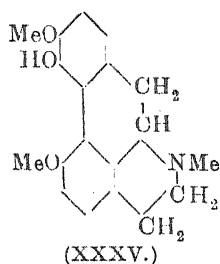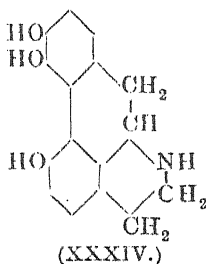
If the hydroaromatic ring of XXXII becomes oxidised, as may well happen simultaneously with the *N*-methylation of formaldehyde, one of the ·CH(OH)· groups becoming ·CO·, then elimination of water leads to XXXVI, which by methylation and methylenation provides numerous alkaloids of the corydalis–phenanthrene type, such as bulbocapnine (XXXVII) (Gadamer and Kuntze, *Arch. Pharm.*, 1911, **249**, 598).

(XXXVI.)   (XXXVII.)   (XXXVIII.)
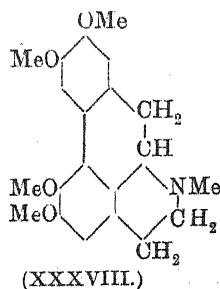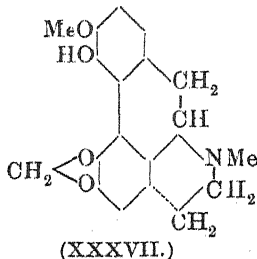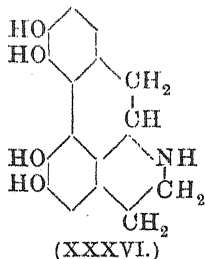
In glaucine (XXXVIII) and dicentrine (Asahina, *Arch. Pharm.*, 1909, **247**, 201; Gadamer, *ibid.*, 1911, **249**, 680) the orientation of the catechol ether groups suggests that these bases are the result

of condensation of the aromatic aldehyde (XXVIII) with the hydroaromatic base (XXV), and the condensation which closes the phenanthrene ring may then produce a 4:5-substituted catechol derivative. Apart from this, the reactions necessary will entirely resemble those required for bulbocapnine.

E. *Norlaudanosine and the Products obtained from it by the Action of Formaldehyde.*—Norlaudanosine (XXXIX) is the result of condensation of XXVII and XXVIII, as illustrated below (compare Winterstein and Trier, *loc. cit.*, p. 307):
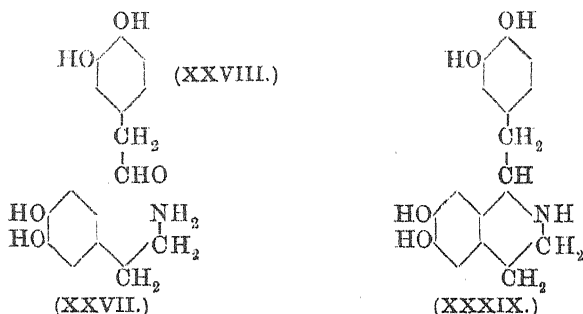
Norlaudanosine is subject to attack by formaldehyde at six points, and the nature of the substances produced largely depends on the amount of oxidation which accompanies the methylations.

(*a*) *Laudanosine*,

$$C_{16}H_{17}O_4N + 5CH_2O = C_{21}H_{27}O_4N + 5O.$$

Complete methylation of phenolic hydroxyls and of the imino-group unaccompanied by internal oxidation.

(*b*) *Papaverine*,

$$C_{16}H_{17}O_4N + 4CH_2O = C_{20}H_{21}O_4N + 2O + 2H_2O.$$
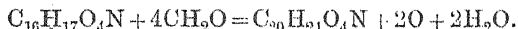
Methylation of phenolic hydroxyl and oxidation of the tetra-hydro*iso*quinoline ring.

(*c*) *Xanthaline (papaveraldine)*,

$$C_{16}H_{17}O_4N + 4CH_2O = C_{20}H_{19}O_5N + 3H_2O.$$

(*d*) *Hydrastine*,

$$C_{16}H_{17}O_4N + 5CH_2O = C_{21}H_{21}O_6N + 3H_2O.$$
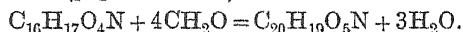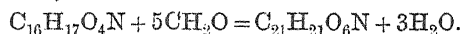
The essential reaction here is a "Lederer-Manasse" synthesis, introducing the group $\cdot CH_2 \cdot OH$ into the benzene ring. The product then becomes simultaneously methylated and oxidised, as indicated below:
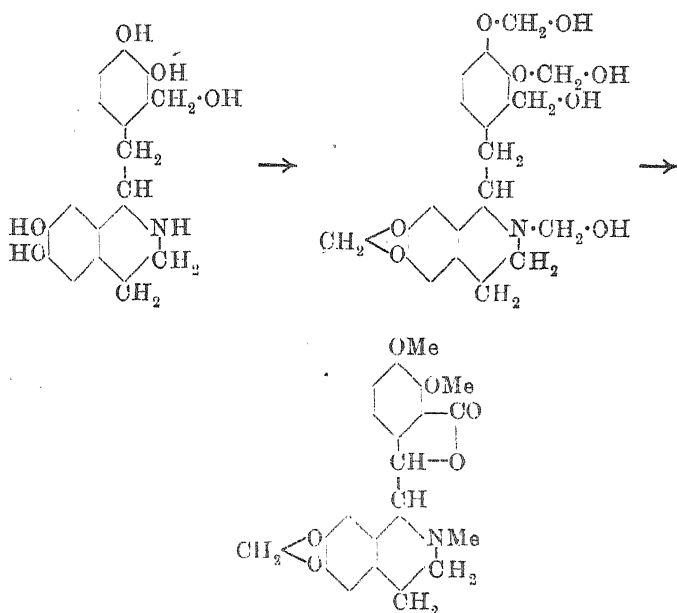
(e) *The Berberine Sub-group.*

The establishment of a bridge between the nitrogen and the benzene ring produces norcanadine (XL), and the reaction is, of course, that which Pictet and Gams (*Compt. rend.*, 1911, **153**, 386; *Ber.*, 1911, **44**, 2480) devised for the synthesis of tetrahydroberberine:
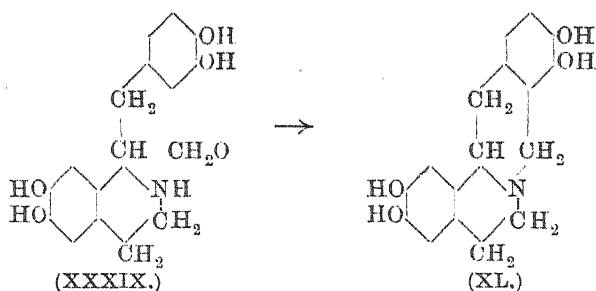
From norcanadine the following are obtained by the action of formaldehyde:

(a) *Canadine,*

$$C_{17}H_{17}O_4N + 3CH_2O = C_{20}H_{21}O_4N + 2O + H_2O.$$
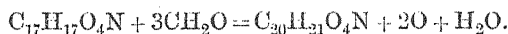
Methylation of two phenolic hydroxyls and methylenation of two more.

(β) *Berberine*,

$$C_{17}H_{17}O_4N + 3CH_2O = C_{20}H_{19}O_5N + 2H_2O.$$
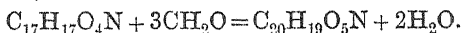
The same processes as with canadine, using the oxygen for the conversion of the tetrahydro*iso*quinoline derivative into a true alkyl*iso*quinolinium hydroxide.

(γ) *Protopine*,

$$C_{17}H_{17}O_4N + 3CH_2O = C_{20}H_{19}O_5N + 2H_2O.$$
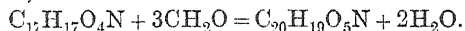
Complete methylenation of norcanadine yields XLI, and the action of formaldehyde on this substance may produce protopine (XLII) (Perkin, T., 1916, **109**, 875).

(XLI.)   (XLII.)
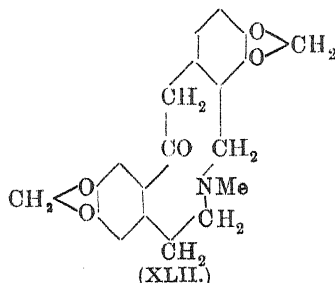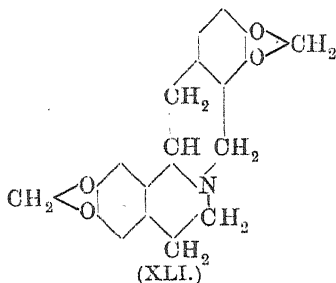
This is a reaction of a more hypothetical character than any other introduced in this communication, but since a ring-scission in this direction of tetrahydroberberine methohydroxide has been established by Pyman (T., 1913, **103**, 828) and since these results have been paralleled in the *iso*tetrahydroberberine series in connexion with derivatives of cryptopine (Perkin, *loc. cit.*, p. 841) there appears to be little improbability in the assumption, and the details of the process may follow the partial scheme:

(δ) *Cryptopine* (Perkin, *loc. cit.*, p. 831),

$$C_{17}H_{17}O_4N + 4CH_2O = C_{21}H_{27}O_5N + 2O + H_2O.$$
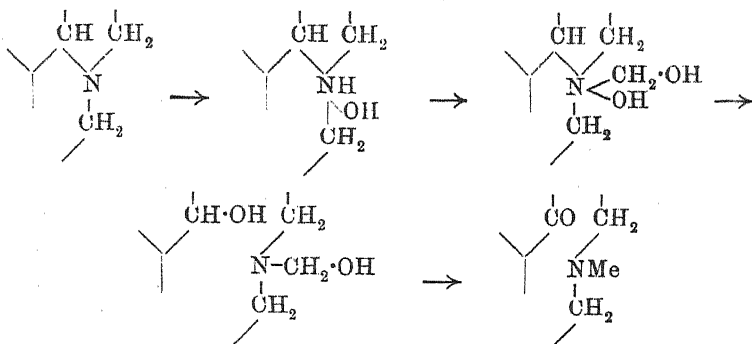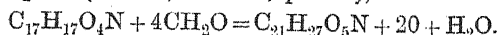
This would result from norcanadine by methylation and methyl-

enation to form an *iso*tetrahydroberberine, which might yield the base by the further action of formaldehyde as with protopine.

F. *Narcotine and Narceine.*—3 : 4-Dihydroxyphenylacetaldehyde (XXVIII) and the base XXIX are supposed to condense with formation of the methylene ether of hydroxy-*N*-methylnorlaudanosine (XLIII), which is converted into narcotine (XLIV) in precisely the manner employed above in the case of hydrastine. The ring-scission of narcotine with the formation of narceine is similar to the production of protopine and cryptopine, except that the further methylation of the nitrogen is not accompanied by internal oxidation :

(XLIII.)

(XLIV.)
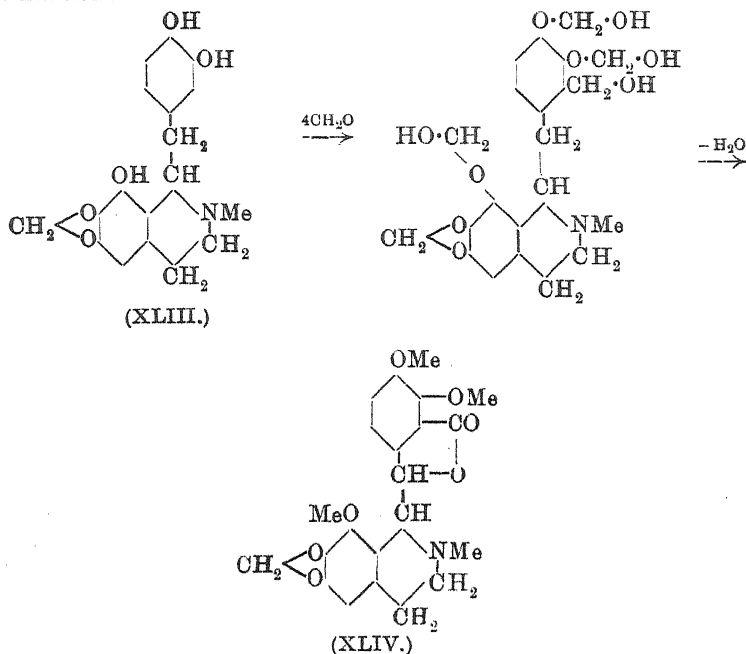
G. *Corydaline.*—Notwithstanding the observation of Gadamer (*Arch. Pharm.*, 1915, **253**, 274) that corydaline loses its optical activity when it is oxidised to didehydrocorydaline, and that therefore the two asymmetric carbon atoms should be contiguous, an alteration in the accepted formula of the alkaloid cannot be considered. Especially is the position of the methyl group clearly proved by the arguments of Dobbie and Lauder (T., 1902, **81**, 154) relating to the methylpyridinetricarboxylic acid obtained by them from corydic acid, although a slight modification of the constitution of the latter substance would now be made so as to represent it as a true pyridine derivative and as a betaine (compare Perkin, *loc. cit.*, p. 836).

Corydaline accordingly appears as a methylated norlaudanosine with an ethylidene bridge between the nitrogen atom and the aromatic nucleus, a structure produced by the intervention of acetaldehyde instead of formaldehyde. Attention may be again directed to the possibility that what may be termed the hemipinic orientation may result from aldol condensation with the hydroaromatic progenitors of these alkaloids, whilst the metahemipinic orientation is to be expected if the condensations are subsequent to the conversion of the hydroaromatic compounds into catechol derivatives by loss of water.

H. *The Conditions affecting the Production of the* iso*Quinoline Bases.*—The problem may be put in the form of a question : Why do not alkaloids assumed as above to have a common origin always occur together in the plant ? Why, for example, does not morphine occur in *Hydrastis canadensis*? It is reasonable to expect some answer to this, but not, in the circumstances, a complete one. In the particular case mentioned the scheme shows that the molecule must suffer reduction before morphine can be obtained. That there are reducing conditions is clear also from the formation of laudanosine. On the other hand, the formation of hydrastine and of berberine follows such a course that all the oxygen available from the methylations is used internally, and powerful reducing agents would therefore appear to be absent during the formation of these bases. This would be sufficient to account for the non-production of morphine. Among other circumstances that may affect the nature of the end-products are the stereochemical relations of the hydroaromatic substances, the rapidity with which these lose water with the formation of aromatic compounds, the stage at which N-methylation occurs, the concentration of formaldehyde and other reagents, the presence or absence of enzymes and other catalysts, all of which are without doubt connected with the needs of the plant itself. If these varying conditions are taken into account the objection that the simplicity of the schemes proves too much cannot well be sustained.

Some of the more remarkable coincidences encountered in the development of the foregoing suggestions may now be noted in summary and conclusion. In the pyrrolidine group hygrine, cuschygrine and tropinone are related by their method of formation, and by introducing a piperidone ring into hygrine by means of a reaction entirely similar to that required for sparteine it is seen that an explanation is provided of the β-position of the pyrrolidine complex in the pyridine nucleus of nicotine. In the piperidine group the methods are homologous with those of the pyrrolidine group and the nature of the reduced pyridine derivatives

which have been obtained from plants is quite in harmony with the origin from lysine.   In particular, the α-propyl chain of coniine is explicable on the assumption that it represents a reduced acetone residue.   In the quinuclidine group the bridged rings of sparteine and quinine are produced by similar methods, the application of which fixes the position of the connecting methylene group of sparteine and the vinyl group of quinine.   Substances accompanying quinine and cinchonine in cinchona-bark have been found to be suitable starting points for a synthesis of the quinoline-half of the molecules of these alkaloids.   In the *iso*quinoline group it is noteworthy that one and the same hypothetical hydroaromatic substance derived in part from a carbohydrate degradation product also required for quinine, suffices for the production of the whole of the bases of the group the constitutions of which have been elucidated.   It is hoped that it will prove possible to employ this theory as a working hypothesis in several directions.

THE UNIVERSITY,
    LIVERPOOL.   [*Received, July 23rd,* 1917.]

LXXVI.—*Reduction of Aliphatic Nitrites to Amines.*

By PANCHĀNAN NEOGI and TARINI CHARAN CHOWDHURI.

NEOGI and Chowdhuri have shown (T., 1916, **109**, 701) that aliphatic nitrites are partly converted into the corresponding nitro-compounds by the action of heat.   The conversion commences at about 100°, and the best results are obtained at 125—130°.   If, however, the temperature is further raised, secondary reactions take place, and, in addition to nitro-compounds, aldehydes and acids are formed.

By the reduction of aliphatic nitrites in solution, alcohol and hydroxylamine or ammonia are obtained, but as the nitrites are partly converted into nitro-compounds on heating, it follows that on reducing them at a higher temperature, amines should be produced in addition to ammonia.   Gaudion has shown (*Ann. Chim. Phys.,* 1912, [viii], **25**, 125) that amines are obtained by the reduction of aliphatic nitrites with heated, finely divided nickel or copper.   The temperature employed by him, however, was very high, namely, above 220° in the case of nickel and above 300° in the case of copper, temperatures at which the nitrites decompose, giving secondary products.   He therefore obtained a mixture of mono-, di-, and tri-alkylamines in the reaction.   We have,

however, made experiments at as low a temperature as 100—130°, and have been able to show that the corresponding monoalkyl-amine alone is obtained, thus conclusively proving that the resultant amine is the direct product of reduction of the nitro-compound, best formed at 125—130°, as previously shown by us.

That nitro-compounds are reduced to amines when a mixture of hydrogen and the nitro-compounds is passed over heated nickel has already been shown by Sabatier and Senderens (*Compt. rend.*, 1902, **135**, 226).

<center>EXPERIMENTAL.</center>

A slow stream of pure hydrogen was passed through a flask containing the aliphatic nitrite, and the mixture of hydrogen and nitrite vapour then passed into a combustion tube, about 90 cm. in length, filled with reduced nickel and heated in an asbestos box provided with a thermometer. The air was first expelled by the current of hydrogen, and then the mixture of the two gases allowed to pass into the tube. To the other end of the tube was attached a dry test-tube, immersed in cold water and connected in its turn with two Erlenmeyer flasks containing dilute hydro-chloric acid. Liquid products of reduction, such as alcohols and part of the liquid amines, collect in the test-tube, whilst the vapour of the escaping amines, especially in the case of the lower members, and ammonia, are arrested in the hydrochloric acid flasks.

The liquid in the test-tube, which gave the pungent, fishy odour of the amines, was neutralised with hydrochloric acid and the alcohol distilled off. The alcohol was recognised by its odour and identified by determining the boiling point of its acetate.

The hydrochloride of the amine and ammonia in the Erlen-meyer flasks and in the test-tube after distilling off the alcohol was evaporated to dryness. The amine hydrochloride was separated from ammonium chloride by repeated exhaustion with small quantities of absolute alcohol and ether. Besides recog-nising the amines by Hofmann's carbylamine reaction and other characteristic tests, they were identified quantitatively by pre-paring their platinichlorides. Analysis of these showed that monoalkyl-, and not di- or tri-alkyl-amines were formed.

One point is important in the preparation of the amine platini-chlorides in the presence of ammonia. It is known that even on repeated exhaustion of a mixture of amine hydrochloride and ammonium chloride with alcohol and ether, the amine hydro-chloride is not obtained free from ammonium chloride. On the addition of platinic chloride, however, to a moderately dilute

solution of the salts, the precipitate which is first produced contains all the remaining ammonium chloride, together with a little amine hydrochloride. If now platinic chloride is added to the filtrate and the solution concentrated, if necessary, shining, yellow crystals are formed consisting solely of the amine platinichloride.

The use of reduced nickel in the powder form, as employed by Sabatier and Senderens, was not satisfactory. The powder forms a layer inside the glass tube, and evidently does not present a sufficiently large surface of contact for the action of the gases. We therefore prepared *nickelised asbestos* by first soaking asbestos fibre in a concentrated solution of nickel nitrate, then drying, and heating it in the blow-pipe in a large nickel basin in order to convert the nitrate into the oxide. The glass tube was then filled with the asbestos impregnated with nickel oxide, placed in an inclined position, and heated at about 300° in a current of hydrogen, when the oxide was reduced to metallic nickel. The nickelised asbestos, with which a tube can be fully packed, is strongly recommended whenever reduced nickel is necessary for work with gases, as it presents a very large surface for the reacting gases with the use of a comparatively small quantity of nickel. When once prepared, the nickelised asbestos may be used over and over again.

The experiments here described were also repeated with reduced iron, but the results were much less satisfactory.

isoAmylamine from isoAmyl Nitrite.

The products from six experiments, in each of which 4 c.c. of the nitrite were used, were united. The temperature employed was 125—130°:

Amine hydrochloride $= 1·6$ grams

Ammonium chloride $= 3·4$ „

Analysis of the platinichloride of the amine gave $Pt = 33·61$, whereas *iso*amylamine platinichloride requires $Pt = 33·39$ per cent.

The acetate of the alcohol was prepared, and identified as *iso*amyl acetate by its boiling point (137—138°).

isoButylamine from isoButyl Nitrite.

Seven experiments were performed at 125—130°, using 4 to 5 c.c. of nitrite in each case:

Amine hydrochloride $= 1·9$ grams.

Ammonium chloride $= 3·2$ „

N N 2

Analysis of the platinichloride gave Pt = 35·23; calc., Pt = 35·07 per cent.

isoButyl acetate was prepared from the alcohol, and identified by its boiling point (116—117°).

N-*Propylamine from* n-*Propyl Nitrite.*

Six experiments were made at 130°, using the same quantities as in the previous experiments:

Amine hydrochloride = 1·3 grams.

Ammonium chloride = 2·9 ,,

Analysis of the platinichloride gave Pt = 37·10; calc., Pt = 36·93 per cent.

The acetate of the alcohol boiled at 102°, showing that the alcohol was *n*-propyl alcohol.

Ethylamine from Ethyl Nitrite.

As ethyl nitrite is gaseous at the ordinary temperature, it was dissolved in paraffin oil, and a 25 per cent. solution was used. As the nitrite is very volatile, even in solution, much escaped without reduction.

As a result of six experiments, using 5 c.c. of the solution each time, ethylamine hydrochloride (0·62 gram) and ammonium chloride (3·2 grams) were obtained. Analysis of the platinichloride gave Pt = 39·23; calc., Pt = 39·00 per cent.

Ethyl alcohol was detected by the iodoform, morphine, and other tests.

Methylamine from Methyl Nitrite.

Methyl nitrite was prepared according to the directions given in our previous paper (*loc. cit.*) and dissolved in paraffin oil. Much of the nitrite escaped reduction, owing to its volatility. About 0·10 gram of the amine hydrochloride was obtained as the result of six experiments. Owing to the low yield of the amine salt and to the presence of much ammonium chloride, analysis of the small quantity of the platinichloride did not give good results.

Methyl alcohol was recognised by the formic acid, morphine, and other tests.

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LXXVII.—*Experiments on the Orientation of Substituted Catechol Ethers.*

By Thomas Gilbert Henry Jones and Robert Robinson.

APPARENT anomalies noted in the course of attempts to prepare 2-nitrohomoveratrole rendered it necessary to examine the whole question of the entry of substituents into the catechol nucleus, and as the matters of interest encountered in the prosecution of the investigation * are of somewhat divergent character they are separately discussed in the ensuing sections.

I. *Substitution in Veratrole or Catechol Methylene Ether and their Derivatives.*

(*a*) In the preparation of monosubstituted catechol ethers only the 4-derivative is obtained. For example, no trace of 3-nitroveratrole is produced in the nitration of veratrole (Cardwell and Robinson, T., 1915, **107**, 257), and only the para-compound is obtained on bromination (see p. 916).

(*b*) Disubstituted catechol ethers are 4:5-derivatives.

The constitution of 4:5-dinitroveratrole may be definitely proved in several ways, of which the simplest depends on the production of the substance from metahemipinic acid by elimination of the carboxyl groups. The disubstituted catechol ethers are therefore connected with 4:5-dinitroveratrole by transformations and inter-conversions as shown below. A number of known substances of hitherto undetermined constitution are included, and in all cases where two specimens are stated to be identical this was proved by direct comparison and by the determination of the melting point of a mixture. This technique is also implied in the statement that a product was identified with a known compound.

There are two well authenticated exceptions to this rule, but the circumstances in both cases are somewhat unusual. Gaspari (*Gazzetta*, 1896, **26**, ii, 231) nitrated bromoveratrole and obtained a substance melting at 125° (I). now shown to be 4-bromo-5-nitro veratrole, but, on brominating nitroveratrole in chloroform solution

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* The investigations described in this and four of the five following communications were made in the laboratories of the University of Sydney during 1914—1915 and were interrupted before they were quite completed, but as there is no immediate prospect of the possibility of further work in these directions it seems undesirable to delay the publication of the results already ascertained.
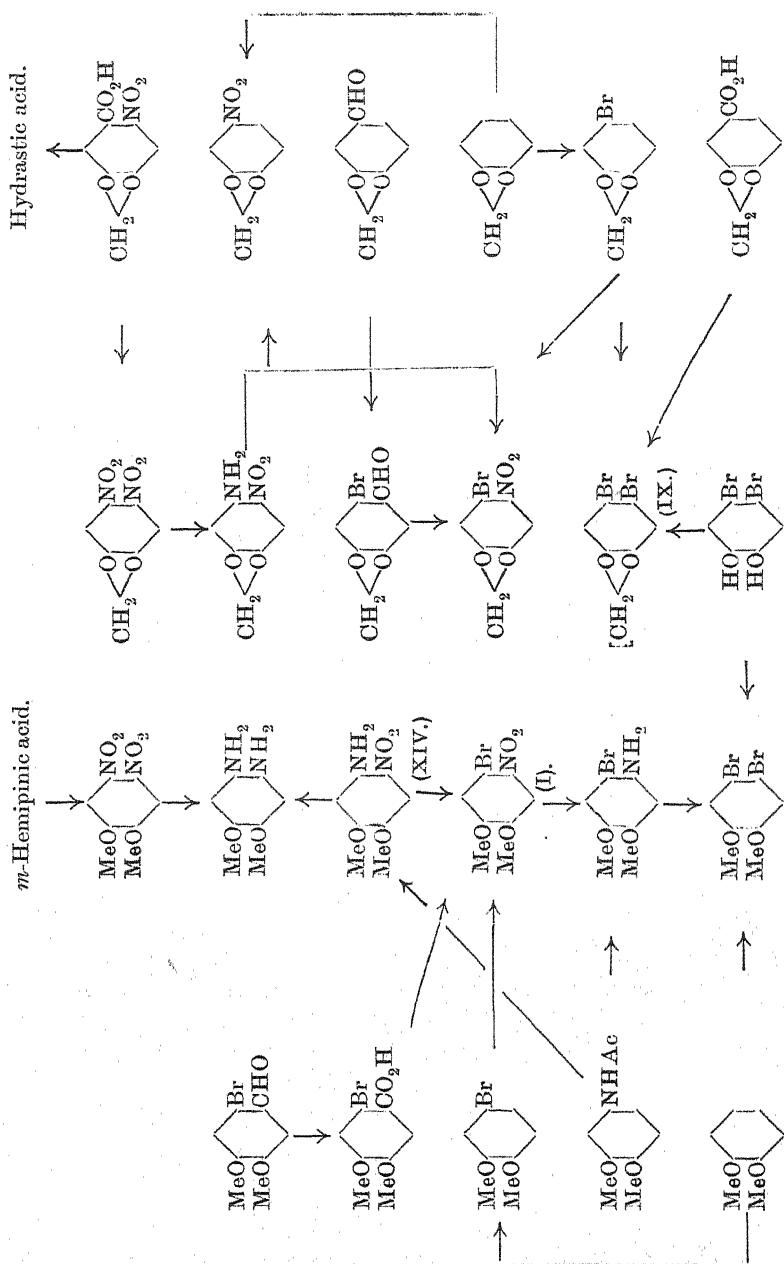
at 100°, Cousin (*Ann. Chim. Phys.*, 1898, [vii], **13**, 504) produced an isomeride melting at 111—112°. The latter reaction has been re-examined and the formation of the isomeride confirmed, although in our experience the main product was a nitrophenol, identified as 6-bromo-4-nitroguaiacol (Meldola and Streatfeild, T., 1898, **73**, 681; Robertson, T., 1908, **93**, 788), which yielded the bromonitro-veratrole (m. p. 112°) on methylation. The bromination of 4-nitro-veratrole leads, therefore, to 6-bromo-4-nitroveratrole. In this case the reaction proceeds with considerable difficulty at 100°, and yet, in view of the tendency to produce 4 : 5-derivatives, it must be conceded that, whatever the mechanism, here is a genuine example of direction by the nitro-group.

A second exception to the rule is found in the synthesis of tetra-hydroberberine by Pictet and Gams (*Compt. rend.*, 1911, **155**, 386; *Ber.*, 1911, **44**, 2430), an anomalous production of a 3 : 4-disubsti-tuted veratrole apparently due to a particular arrangement in space, relative to the imino-group, of the veratrole nucleus in the complicated molecule of which it forms a part.

(c) In the preparation of 3 : 4 : 5-derivatives from a 4 : 5-disubsti-tuted catechol ether the new substituent enters the ortho-position with respect to the more negative of the groups occupying the positions 4 and 5 unless one of these groups is powerfully ortho-direc-tive. The following are examples which occur in the experimental part of the paper:
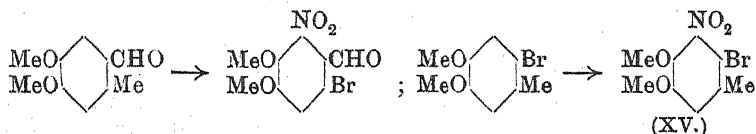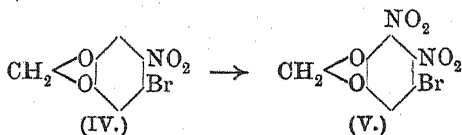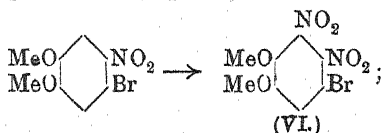
It appears to be generally recognised that the orientating effect of a positive group such as methoxyl is overwhelmingly greater than that of a negative group, such as nitroxyl, and that the influence of negative groups is chiefly felt in diminishing the positive un-saturation of the molecule and so inhibiting further substitutions which owe their occurrence to the reactivity associated with the

unsaturation of the nucleus conjugated (compare this vol., p. 964) with that of the positive centres. When two identical positive groups co-exist in the same molecule and direct substitution to different positions, a means is provided for the examination of the effect of negative groups on their orientating power. The following examples illustrate the weakening effect of a negative group on a positive centre situated in the ortho-position, and those which are cited above are probably due to a similar effect exerted from the para-position.

; Perkin, Roberts, and Robinson (T., 1914, **105**, 2389).

(see page 912).

(XII.)

and

; Blanksma (*Rec. trav. Chim.* 1907, **27**, 49).
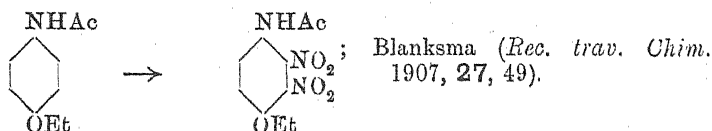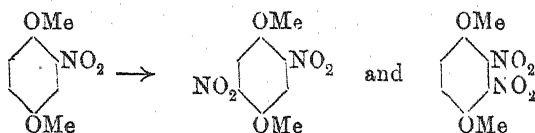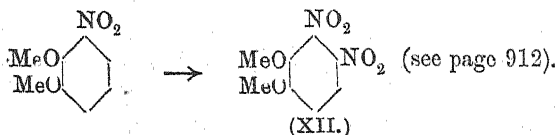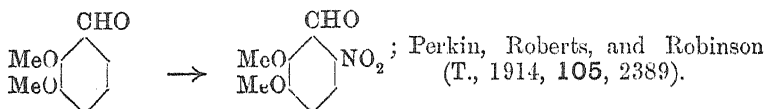
The exceptional behaviour of *o*-veratric acid on nitration (Cain and Simonsen, T., 1914, **105**, 159) has already been adequately discussed by Gibson, Simonsen, and Rau (this vol., p. 73).

II. *The Influence of a Negative Group on a Positive Group in the Meta-position.*

Perhaps the most widely known example of this effect is to be found in connexion with diazo-coupling with *α*-naphthylamine and *α*-naphthol and with their sulphonic acids. The arrows show the position taken up by the entering azo-group:
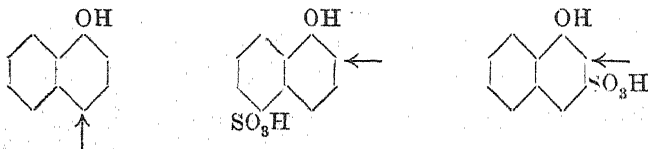
Comparable with this is the behaviour of acetylguaiacol and of acetylvanillin on nitration (Pschorr and Sumuleanu, *Ber.*, 1899, **32**, 3405):

We have observed another example of the same kind, and find that the bromination of 5-nitroguaiacol (see p. 917) produces 6-bromo-5-nitroguaiacol:
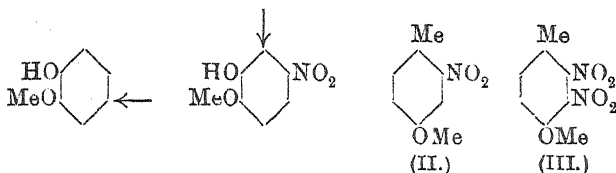
In all these cases an ortho-position is preferred to the para, and it would seem that a negative group in the meta-position to the directive positive group is responsible for the effect. There is evidence, too, that it is not merely an ortho-substitution which is favoured, but that it is the particular ortho-position situated between the positive and negative groups. Thus Kaufler and Wenzel (*Ber.*, 1901, **34**, 2239) observed that 2-nitro-*p*-tolyl methyl ether (II) gave 2 : 3-dinitro-*p*-tolyl methyl ether (III) on nitration, and there are many similar cases which have been recorded. It must further be pointed out that a positive group in the ortho-position has precisely the opposite effect to the meta-situated negative group. An example of this is found above in I (*a*), or in comparing the nitration of acetylvanillin with that of veratraldehyde. In the former case (see above) the nitro-group enters the ortho-position with respect to the methoxy-group, whilst in the latter it enters the para-position and 6-nitroveratraldehyde is produced. It is possible to translate all observations on orientation and cognate problems into the form of expressions which represent the distribution of affinity and the nature of the partly dissociated simple or conjugated unsaturated systems to which the initial additions occur. The more precise presentation of the difficulties which is so obtained is to some extent helpful, but especially in connexion with the effect of group on group the experimental data cannot yet be regarded as sufficient to enable very definite conclusions to be drawn. This is perhaps partly due to the circumstance that the entry of a pronouncedly negative or positive group affects the state of saturation of all the atoms in the molecule, and the difficulty

resembles that which is met in attempting to trace a relation between constitution and physical properties.

III. *The Nitration of Bromopiperonal.*

Oelker (*Ber.*, 1891, **24**, 2593) studied this reaction and stated that the products were bromonitropiperonal melting at 89° and bromodinitropiperonal melting at 172°. These substances are, however, bromonitrocatechol methylene ether (IV) and bromodinitrocatechol methylene ether (V), the aldehydo-group having been eliminated. The latter substance on reduction yields 3 : 4-diaminocatechol methylene ether isolated in the form of a phenanthraphenazine, but, under the same conditions of reduction, the corresponding veratrole derivative (VI) retains its bromine and yields a bromodiaminoveratrole.

IV. *The Action of Nitric Acid on Methylenedioxyisatin.*

Herz (*Ber.*, 1905, **38**, 2857) prepared methylenedioxyisatin by the moderated oxidation with nitric acid of the readily accessible dimethylenetetraoxyindigotin, and represented the further action of nitric acid as resulting in the formation of an acid (VII), which, when heated with aqueous sodium carbonate, lost carbon dioxide with the formation of the nitroamine (VIII):
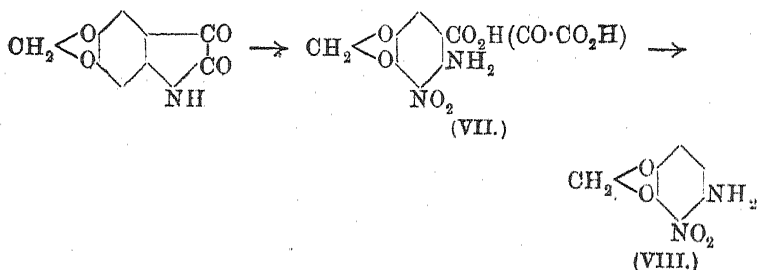
These transformations must, however, be represented in the following manner, since we have identified the product as 5-nitro-4-aminocatechol methylene ether, and find that its production is accompanied by that of sodium oxalate. Moreover, Herz points out that the analytical data for VII agree with the formula $C_9H_6O_7N_2$ almost as well as for $C_8H_6O_6N_2$:
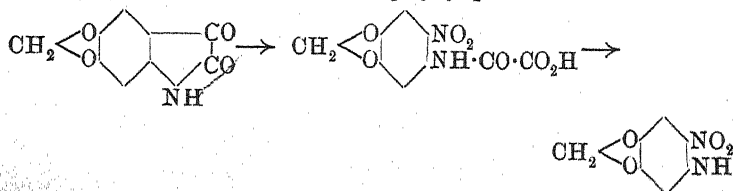
V. *A Reaction of Piperonylic Acid.*

Mr. J. W. Hogarth discovered in 1914 that a crystalline substance melting at 86° is obtained by the action of bromine on a solution of piperonylic acid in aqueous sodium carbonate, and the further investigation of this compound showed that it is 4:5-dibromocatechol methylene ether (IX), and that it is obtained in quantitative amount.

From the conditions requisite for its formation (see p. 913), the conclusion may be drawn that the displacement of the carboxyl group is the first reaction, and that the monobromoderivative is then further brominated. In all probability, the latter stage is rapid in comparison with the former. This view is confirmed by the formation of 6-bromohomoveratrole (see p. 920) by the application of a similar process to 4:5-dimethoxy-*o*-toluic acid, and the reaction is evidently of the same character as that by means of which bromostyrene may be obtained from cinnamic acid. Such displacements are clearly analogous to substitutions and are certainly preceded by addition, whilst the group displaced may be removed by hydrolysis, which is facilitated by much the same conditions that determine the separation of the acetyl group in the preparation of chloroform from acetone. If the following formulæ are compared, it will be seen that there are three factors which should render a group ·CO·R in a hypothetical additive product, such as X, readily removable by hydrolysis, namely, the bromine atom in the α-position and the two double bonds in the ring.

$$Cl_3C-|-COMe$$
$$NO_2\cdot CH_2-|-CO_2H$$

(X.)
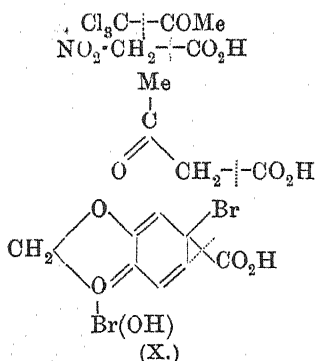
The formation of dibromocatechol methylene ether may be employed as a sensitive test for piperonylic acid, since the colour developed in the sulphuric acid solution of the substance by the addition of a trace of nitric acid is highly characteristic. It is

also probable that the method will be useful in the investigation of acids derived from the alkaloids in degradation experiments, and Professor W. H. Perkin has already found such an opportunity in connexion with a methylpiperonylic acid obtained from cryptopine (T., 1916, 109, 918).

VI. *Phenanthraphenazine Derivatives.*

It has been found to be a general rule that the ethers of 1:2-dihydroxyphenanthraphenazine are bright yellow and exhibit green fluorescence in benzene or other neutral solvent, whilst the ethers of 2:3-dihydroxyphenanthraphenazine are faintly yellow and yield almost colourless solutions with intense violet fluorescence. The latter property can be made the basis of perhaps the simplest method of obtaining an indication that a plant product is a derivative of veratrole substituted only in the 4- or 4:5-positions. A small quantity of the substance is boiled with 40 per cent. nitric acid in such a manner as to ensure vigorous oxidation and concentration of the solution; a further quantity of concentrated nitric acid is then added and the boiling continued for a few minutes. The mixture is added to water and extracted with ether, the extract washed with water and evaporated, and the residue, however small, dissolved in a little alcohol, and after the addition of two or three drops of hydrochloric acid, reduced by zinc dust. The filtered solution is mixed with sodium acetate and a solution of a few crystals of phenanthraquinone in hot aqueous sodium hydrogen sulphite, and, after boiling, is extracted with benzene. The benzene is clarified by means of calcium chloride and filtered, and the fluorescence observed. The reaction may be applied with even more certainty to the products obtained by oxidation with an alkaline solution of potassium permanganate of the substance which is under investigation. Positive results were obtained, using about 0·05 gram of papaverine, trimethylbrazilin, eudesmin, and several synthetical compounds which happened to be in the laboratory at the time the experiments were made. The preparation of 1:2:4-trimethoxyphenanthraphenazine and of the isomeric pyrogallol derivative (see p. 928) confirms the correctness of the constitution assigned by Blanksma (*Proc. K. Akad. Wetensch. Amsterdam,* 1904, **7**, 462) to the dinitrotrimethoxybenzene (m. p. 152°) which he obtained by the action of methyl-alcoholic potassium hydroxide on trinitroveratrole.

VII. *A New Heterocyclic Nucleus.*

On attempting to reduce 4:5-dinitroveratrole to a nitroamine by means of hydrogen sulphide and ammonia, an unusual result

was obtained, and the product was a sparingly soluble orange-yellow, crystalline compound, $C_{16}H_{16}O_6N_4S$, which on reduction furnished a base, $C_{16}H_{18}O_4N_4S$, having the properties of a derivative of veratrylamine (see p. 925). Evidently a nitro-compound has been reduced to the corresponding amine. Bearing in mind the method of formation of the substance $C_{16}H_{16}O_6N_4S$, it seems that the fragments to be combined are

and it then appears that the formula of the substance must be one of the following :

(XI.)

NS   (excluded)

(XII.)

(improbable)
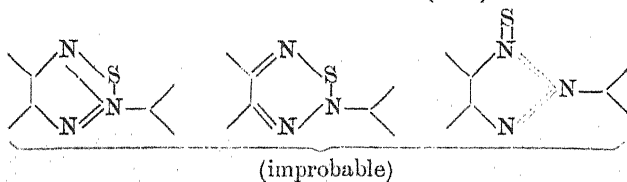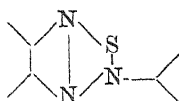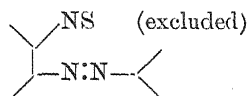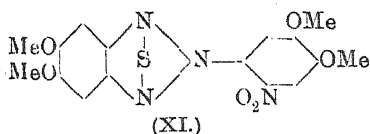
There is no evidence which enables a decisive choice to be made from the various possibilities, but perhaps XI is preferable as being analogous to the constitution now accepted for benzfurazan oxide (XII) (Green and Rowe, T., 1913, **103**, 897; Forster and Barker, *ibid.*, 1918). The whole question of the mode of formation and the properties of these substances will be more closely investigated when opportunity occurs. In the meantime, the SN_3-group has been provisionally designated "thiotriazo," and the substance XI is described as 6-nitroveratryl-4 : 5-thiotriazo-veratrole.

EXPERIMENTAL.

3 : 4-*Dinitroveratrole* (XIII).

3-Nitroveratrole was dissolved in cold nitric acid (D 1·42) and the solution allowed to remain during two hours, and then poured

into water. The precipitated oil soon solidified, and the substance was purified by several crystallisations from methyl alcohol. The pale yellow needles melted at 96° with previous softening, and although obviously not quite pure, the amount of material available was insufficient to enable us to remedy this by a long series of fractional crystallisations:

0·1095 gave 0·1699 CO_2 and 0·0372 H_2O.   C=42·3; H=3·8.
$C_8H_8O_6N_2$ requires C=42·1; H=3·5 per cent.

The substance is readily soluble in most organic solvents and is changed by fuming nitric acid to 3 : 4 : 5-trinitroveratrole. Gibson, Simonsen, and Rau (this vol., 83) have described as 3 : 4-dinitroveratrole a substance melting at 181° which is sparingly soluble in alcohol. In the introduction to their communication, these authors recognise the improbability that 3 : 4-dinitroveratrole can have so high a melting point, but since the molecular weight of the substance was determined they do not reconsider the view advanced. When opportunity offers, attempts will be made to prepare the dinitro-derivative by a new method, and so clear up the question of the melting point. In the meantime, the following experiment proves the constitution of the substance obtained as described above.

The substance (0·5 gram) was dissolved in boiling alcohol (10 c.c.), mixed with concentrated hydrochloric acid (5 c.c.), and an excess of zinc dust added in one portion. After the stormy reaction water was added and the solution filtered, mixed with excess of sodium acetate and with a solution of phenanthraquinone in hot aqueous sodium hydrogen sulphite to which sodium acetate had also been added. The mixture was boiled, and the quinoxaline derivative soon separated in yellow flocks, which were collected, dried, and crystallised from alcohol, and so obtained in long, yellow needles melting sharply at 175°. Pisovschi (*Ber.*, 1910, **43**, 2137) has previously prepared this 1 : 2-dimethoxy-phenanthraphenazine, and the product from 3 : 4-dinitroveratrole agrees in every respect with his description. Like the corresponding methylenedioxy-derivative (compare p. 927), its benzene solution exhibits intense green fluorescence.

6-*Bromoacetoveratrylamide*,   MeO⟨ ⟩NHAc   .
MeO⟨ ⟩Br
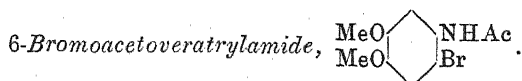
Acetoveratrylamide was brominated in cold acetic acid solution by means of a molecular proportion of bromine. The reaction was almost instantaneous, and, after the addition of water, the

substance was collected and crystallised from methyl alcohol. From a fairly dilute solution a single stellar aggregate of needles, some of them 9 cm. long, was obtained. The melting point was 140°:

0·1332 gave 0·0912 AgBr.   Br = 29·1.

$C_{10}H_{12}O_3NBr$ requires Br = 29·2 per cent.

This substance was converted into 4 : 5-dibromoveratrole in the following manner. The amide (10 grams) was boiled during ten minutes with saturated aqueous hydrobromic acid (25 c.c.), then diluted with water (150 c.c.), cooled to −5°, and the amine contained in the solution diazotised in the usual way. Copper powder was then added, and, after remaining overnight, the reaction was completed by heating on the steam-bath and the whole extracted with ether. The solution was washed with alkali and water, dried, and evaporated, and the residual oil gradually crystallised on keeping in the ice-chest. It was freed from impurity by contact with porous porcelain, and, after crystallisation from alcohol, was obtained in prisms melting at 92—93° identical with the product of bromination of veratrole.

4 : 5-*Dibromocatechol Methylene Ether* (IX).

This compound is readily obtained by adding bromine water to a solution of piperonylic acid in aqueous sodium carbonate until no further precipitate is formed. It may be crystallised from alcohol, and is so obtained in colourless, glistening leaflets melting at 86°, and moderately readily soluble in most organic solvents:

0·1276 gave 0·1703 AgBr.   Br = 56·8.

$C_7H_4O_2Br_2$ requires Br = 57·2 per cent.

The pale yellow solution in sulphuric acid is changed to crimson on the addition of a trace of nitric acid.

The substance is not formed by treatment of an alkaline solution of piperonylic acid with ready-formed hypobromite, or even by the bromination of piperonylic acid in acetic acid solution. Neither can it be obtained by the addition of bromine water to a solution of bromopiperonylic acid in sodium carbonate. Veratric acid did not undergo the reaction so readily as piperonylic acid, but the result was similar and 4 : 5-dibromoveratrole was isolated. It seems probable that the method will be useful in the investigation of carboxylic acids derived from alkaloids and other natural products by oxidation.

4 : 5-Dibromocatechol (Cousin, *loc. cit.*, 487), which yields 4 : 5-dibromoveratrole on methylation, was converted by methylene

iodide and sodium ethoxide in boiling alcoholic solution into 4 : 5-dibromocatechol methylene ether melting at 86°, and identical with the substance obtained as described above. This compound was also produced by the direct bromination of catechol methylene ether in acetic acid solution.

6-Nitroveratrylamine (XIV).

6-Nitroacetoveratrylamide was boiled with concentrated hydrochloric acid until the whole of the yellow needles passed into solution. The pale yellow hydrochloride of the base separated on cooling, and on the addition of much water was decomposed, yielding the orange nitroamine. This was collected and crystallised from alcohol, from which it separated in deep orange prisms melting at 175° :

0·1304 gave 0·2315 CO_2 and 0·0600 H_2O.   C = 48·4 ; H = 5·1.

$C_8H_{10}O_4N_2$ requires C = 48·5 ; H = 5·0 per cent.

The substance could be diazotised, and gave a crimson azocompound by coupling with β-naphthol. When the diazonium bromide prepared in hydrobromic acid solution was treated with copper powder, nitrogen was evolved, and, after completing the reaction by gentle heating, the neutral substance formed was isolated and identified with 4-bromo-5-nitroveratrole, melting at 125°.

Acetyl Derivative.—Acetoveratrylamide (10 grams) in acetic acid (50 c.c.) was nitrated in the cold by the addition of nitric acid (10 c.c., D 1·42) in acetic acid (50 c.c.). The bright yellow product of the reaction separated for the most part in the crystalline condition, and, after the addition of water, was collected and recrystallised from alcohol, in which the substance is somewhat sparingly soluble. It was obtained in long needles melting at 199° :

0·1258 gave 0·2326 CO_2 and 0·0592 H_2O.   C = 50·4 ; H = 5·2.

$C_{10}H_{12}O_5N_2$ requires C = 50·0 ; H = 5·0 per cent.

5-Nitro-4-acetylaminocatechol Methylene Ether,

$$CH_2 <^O_O \bigcirc ^{NHAc}_{NO_2} .$$
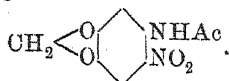
This derivative is obtained in theoretical amount when 4-acetylaminocatechol methylene ether is nitrated in cold acetic acid solution. After the addition of water, the substance was collected and crystallised from acetic acid, and then from ethyl acetate.

The bright yellow needles melt at 209°, and the compound is sparingly soluble in boiling alcohol:

0·1247 gave 0·2207 CO_2 and 0·0419 H_2O.   C = 48·3 ; H = 3·7.
$C_9H_8O_5N_2$ requires C = 48·2 ; H = 3·6 per cent.

In view of the results of Herz (*loc. cit.*), which are discussed on p. 908, it is interesting to note that this amide is readily hydrolysed by alkaline agents and even by a boiling solution of sodium carbonate, but the more convenient method is to employ hydrochloric acid diluted with half its volume of alcohol. The acetyl derivative is finely powdered and treated with the boiling mixture until a homogeneous solution is obtained. On the addition of water, an orange, crystalline precipitate of pure 5-nitro-4-aminocatechol methylene ether separates, and, after crystallisation from benzene, the substance melts at 198° and is identical with the compound obtained by Herz and also by Mameli (*Gazzetta*, 1909, **39**, ii, 172) by the action of alcoholic ammonia on 4:5-dinitrocatechol methylene ether. The amine is most easily obtained by a modification of Herz's process, starting with nitropiperonal. The nitroaldehyde (80 grams), dissolved in acetone (240 c.c.), was heated on the steam-bath during half an hour with aqueous *N*-potassium hydroxide (750 c.c.). The paste of the indigotin derivative was collected and washed, and gradually added with stirring to nitric acid (150 c.c., D 1·42) and water (100 c.c.). The oxidation may be induced at first by gentle warming, after which the further application of heat is disadvantageous. The product was collected and washed with water, and then boiled during five minutes with a solution of sodium carbonate (50 grams) in water (500 c.c.). The nitroamine was precipitated in the crystallised condition, and was separated and purified by solution in concentrated hydrochloric acid and recovery by dilution with water. 5-Nitro-4-aminocatechol methylene ether may be recovered unchanged after being boiled with acetic anhydride, but in the presence of a trace of sulphuric acid the acetylation is rapid and the derivative crystallises from the solution. The nitroamine is attacked by hot aqueous sodium hydroxide, and a blood-red solution is produced, but the reaction is complex and unaccompanied by evolution of ammonia.

5 : 6-*Methylenedioxy-2-methylbenziminazole,*
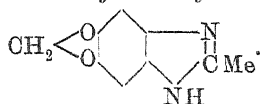
5-Nitro-4-acetylaminocatechol methylene ether (1 gram) was reduced during an hour by heating on the steam-bath with acetic acid (25 c.c.), stannous chloride (0·5 gram), and excess of tin. After one or two minutes, a tin compound separated from the solution in colourless crystals, but this gradually disappeared, and at the end of the operation the liquid had a pale yellow colour. Water and sodium hydroxide sufficient to redissolve the precipitate were added, and the solution was twice extracted with ether. The combined extracts were dried with potassium carbonate and evaporated, and the crystalline residue purified by several re-crystallisations from benzene. The colourless, transparent leaflets so obtained appear to contain solvent of crystallisation, and became opaque on exposure to the air. The substance was dried at 100°:

0·1113 gave 0·2490 CO_2 and 0·0463 H_2O.   C = 61·0; H = 4·6.

$C_9H_8O_2N_2$ requires C = 61·3; H = 4·5 per cent.

This base is sparingly soluble in ether, benzene, or light petroleum, but dissolves freely in methyl alcohol and also to some extent in hot water, from which it crystallises in needles. It melts at 226—227° after sintering at 223°. The *hydrochloride* is readily soluble in water, but may be precipitated in needles by saturation of the solution with salt. The *hydrogen oxalate* is sparingly soluble and crystallises from water in characteristic, satiny plates. The *picrate* crystallises from methyl alcohol in canary-yellow clusters of long needles. It is sparingly soluble and carbonises between 230° and 250° without sudden decomposition.

4-*Bromo*-5 : 6-*dinitroveratrole* (VI).

A quantitative yield of 4-bromo-5-nitroveratrole is obtained by the nitration of bromoveratrole in acetic acid solution (compare Gaspari, *loc. cit.*), and on fractionally crystallising the product it was found to be perfectly homogeneous, and consequently the bromoveratrole is also homogeneous and contains no 3-bromo-veratrole. 4-Bromo-5-nitroveratrole may also be obtained by the action of nitric acid (D 1·42) on that bromoveratric acid which results from the hydrolysis of brominated methyl veratrate or from the oxidation of bromoveratraldehyde. Gaspari (*loc. cit.*) obtained

the dinitro-derivative by the action of fuming nitric acid on bromoveratrole, but from the point of view of yield it is better to isolate the bromomononitroveratrole and submit this substance to the action of cold fuming nitric acid (D 1·52). In this way, the amount obtained approximates closely to that demanded by theory. The constitution of this substance is proved by its conversion into a bromodimethoxyphenanthraphenazine, as described on p. 928.

6-*Bromo*-5-*nitroguaiacol*, $\begin{array}{c} \text{MeO} \\ \text{HO} \end{array} \bigcirc \text{NO}_2$.
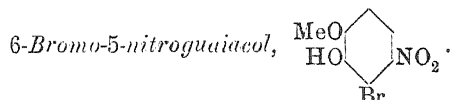
5-Nitroguaiacol (5 grams) dissolved in acetic acid (50 c.c.) was brominated by the gradual addition of bromine (5 grams) dissolved in acetic acid (20 c.c.). After half an hour, the mixture was diluted with water, and the solid collected and recrystallised from aqueous alcohol. The substance is obtained in pale yellow needles, which become prisms if allowed to remain in contact with the solvent, and in either crystalline condition melts at 150° :

0·1364 (0·1206) gave 0·1032 (0·0913) AgBr. Br = 32·2 (32·2).
$C_7H_6O_4NBr$ requires Br = 32·3 per cent.

The substance is readily soluble in aqueous sodium carbonate to a red solution.

6-*Bromo*-5-*nitroveratrole*, $\begin{array}{c} \text{MeO} \\ \text{MeO} \end{array} \bigcirc \text{NO}_2$.
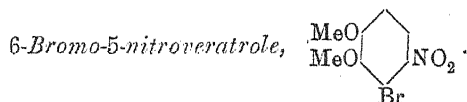
The foregoing bromonitroguaiacol was methylated by shaking its warm solution in aqueous sodium hydroxide with methyl sulphate. The pale yellow substance was collected and crystallised from alcohol. The slender needles melted at 81—82°, and when mixed with specimens of 5 : 4- and 6 : 4-bromonitroveratroles the melting point was depressed :

0·1175 gave 0·0840 AgBr. Br = 30·4.
$C_8H_8O_4NBr$ requires Br = 30·5 per cent.

This substance is rather readily soluble in organic solvents, and dissolves in sulphuric acid to a bright red solution, from which it may be recovered unchanged on the addition of water.

Bromination of 4-Nitroveratrole. Formation of 6-Bromo-4-nitroguaiacol and of 6-Bromo-4-nitroveratrole.

4-Nitroveratrole (10 grams), chloroform (20 c.c.), and bromine (9 grams) were heated together during forty-eight hours in a

sealed tube placed in boiling water. After the reaction, ether was added and the solution shaken with concentrated aqueous sodium hydroxide. The precipitated sodium salt was collected, washed with ether, dissolved in water, and acidified with hydrochloric acid. The separated nitrophenol was collected and crystallised from alcohol and again from benzene, and obtained in pale yellow, glistening needles, which melted at 150—152° with some decomposition, and was identified with 6-bromo-4-nitroguaiacol, which Meldola and Streatfeild (*loc. cit.*) obtained by the bromination of 4-nitroguaiacol, and which was also prepared by Robertson (*loc. cit.*) by nitrating o-bromoguaiacol. The melting points assigned to the substance by these authors are respectively 142° and 148°.

The ethereal solution from the separation of the sodium salt was well washed with water, dried, and evaporated. The residue was fractionally crystallised at first from methyl alcohol and later from ethyl alcohol, and separated into unchanged nitroveratrole and a small proportion of the more sparingly soluble 6-bromo-4-nitroveratrole, which crystallised in slender needles melting at 112—113°.

The substance is more readily obtained by methylating 6-bromo-4-nitroguaiacol by means of methyl sulphate in the usual manner.

4-*Bromo-5-nitrocatechol Methylene Ether* (IV).

This substance has been prepared by Oertly and Pictet (*Ber.*, 1910, **43**, 1336) by the action of nitric acid on bromopiperonylic acid, and an identical compound is obtained by the nitration of an acetic acid solution of bromocatechol methylene ether produced in its turn by the bromination of catechol methylene ether dissolved in acetic acid by means of bromine vapour (from 1·2 mols. of bromine) diluted with air.

Another method of preparation depends on the displacement of the amino-group of 5-nitro-4-aminocatechol methylene ether by bromine by means of the diazo-reaction. The amine was dissolved in concentrated aqueous hydrobromic acid and diazotised by the addition of sodium nitrite, until a clear solution was obtained on treating a test portion with water. The solution was diluted, treated with copper powder, and allowed to remain overnight, and then extracted with ether. The bromonitrocatechol methylene ether which passed into the ether was obtained by evaporation of the solvent and crystallisation of the residue from alcohol. The pale yellow needles melted at 89°, and the substance was identical with the compounds obtained by the other methods here described

The most convenient process for the production of this substance is, however, the nitration of bromopiperonal.

The reaction proceeds in acetic acid solution, but it is better to add the aldehyde (15 grams) gradually to nitric acid (100 c.c., D 1·42) during an hour with careful cooling. The product partly crystallises from the solution, and, after the addition of water, may be collected and crystallised from alcohol. The yield of pure bromonitrocatechol methylene ether melting at 89°, and quite identical with the substance obtained as described above, is very good, and there can be no doubt that this is the substance which Oelker (*loc. cit.*) recorded as a bromonitropiperonal. The following analyses were made of this nitration product of bromopiperonal:

0·1312 gave 0·1657 CO_2 and 0·0237 H_2O.   C = 34·4; H = 2·0.

0·1306 ,, 0·0983 AgBr. Br = 32·1.

$C_7H_4O_4NBr$ requires C = 34·2; H = 1·6; Br = 32·5 per cent.

4-*Bromo*-5 : 6-*dinitrocatechol Methylene Ether.*

This derivative may be obtained directly from bromopiperonal or, better, from bromonitrocatechol methylene ether by dissolving either in an excess of cold nitric acid (D 1·52). The sparingly soluble substance crystallises from ethyl alcohol in pale yellow, prismatic needles melting at 172°, which is the melting point assigned by Oelker (*loc. cit.*) to his supposed bromodinitropiperonal:

0·1437 gave 0·1534 CO_2 and 0·0153 H_2O.   C = 29·1; H = 1·2.

0·1527 ,, 0·0982 AgBr. Br = 27·4.

$C_7H_3O_6N_2Br$ requires C = 28·9; H = 1·0; Br = 27·5 per cent.

6-*Bromo*-5-*nitrohomoveratrole* (XV).

Bromine (7 c.c.) dissolved in acetic acid (50 c.c.) was added to a mixture of homoveratrole (20 grams) and acetic acid (10 c.c.). Rise of temperature was checked during the addition, and the halogen was rapidly absorbed and the product isolated in the usual manner. 6-*Bromohomoveratrole* is an oil with a pleasant aromatic odour, and boils at 267°:

0·1422 gave 0·1153 AgBr. Br = 34·5.

$C_9H_{11}O_2Br$ requires Br = 34·6 per cent.

Attempts were made to bring this substance into reaction with magnesium in order to facilitate the synthesis of *m*-hemipinic acid, but without success.

The bromo-derivative (20 grams) in acetic anhydride (40 c.c.)

was cooled in ice water, and a previously prepared, well-cooled mixture of nitric acid (15 c.c., D 1·42) and acetic anhydride (40 c.c.) gradually added. After half an hour, the reaction mixture was poured into water and the precipitated oil washed with several changes of dilute aqueous sodium hydroxide. The oil soon solidified, and was collected and crystallised from methyl alcohol, from which it separated in long, pale yellow needles melting at 121°:

0·1520 gave 0·1029 AgBr. Br = 28·8.

$C_9H_{10}O_4NBr$ requires Br = 29·0 per cent.

The constitution of this substance is deduced in the following manner. Bromohomoveratrole is oxidised by warm alkaline potassium permanganate solution to 6-bromoveratric acid, which, however, was not identified as such, but was converted by nitric acid into 4-bromo-5-nitroveratrole. The bromination product of homoveratrole is therefore 6-bromohomoveratrole, and the nitro-group in the derivative must occupy either the position 5 or 2. That the substance is not an o-nitrotoluene is shown by the fact that it does not contain an activated methyl group, and, for example, will not condense with cotarnine in alcoholic solution in the presence of sodium ethoxide. In connexion with another investigation, one of us has recently prepared 2-nitrohomoveratrole, and this may be converted into an anhydrocotarnine derivative. Moreover, since the introduction of halogens usually increases the facility with which such condensations are effected, it seems that the bromonitrohomoveratrole must have the constitution here assigned to it. The formation of this substance was utilised in order to show that the action of bromine on a solution of 4:5-di-methoxy-o-toluic acid (Perkin and Weizmann, T., 1906, 99, 1651) in aqueous sodium carbonate leads to the quantitative formation of 6-bromohomoveratrole. The authors are greatly indebted to Professor W. H. Perkin for the provision of a specimen of the acid in question.

6-*Bromo-2-nitroveratraldehyde*,
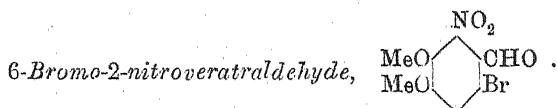
6-Bromoveratraldehyde was nitrated by slowly adding the powdered substance to ten times its weight of nitric acid (D 1·42), checking undue rise of temperature by cooling in water, and, when the solid had passed into solution, the mixture was allowed to remain during half an hour and then poured into water. The precipitate was collected and dissolved as far as possible in a

solution of sodium hydrogen sulphite. The residue was crystallised from alcohol, and the pale yellow needles were identified as 4-bromo-5-nitroveratrole, melting at 124°. The amount of this substance which was obtained was relatively small. The hydrogen sulphite solution was decomposed by the addition of sodium carbonate, and the precipitated aldehyde collected and crystallised from alcohol. The very pale yellow needles melted at 109°:

0·1259 gave 0·0809 AgBr. Br = 27·3.

$C_9H_8O_5NBr$ requires Br = 27·6 per cent.

The constitution of this substance is demonstrated by the formation of the indigotin derivative described in the next section.

$4 : 4'$-*Dibromo*-$6 : 7 : 6' : 7'$-*tetramethoxyindigotin*,
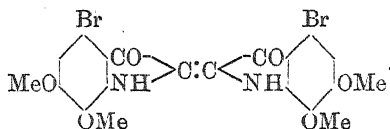
The bromonitroveratraldehyde (4 grams) was dissolved in acetone (30 c.c.) and aqueous potassium hydroxide (5 c.c. of 10 per cent.) added. After a minute, the mixture was diluted with water (100 c.c.) and boiled during five minutes. The precipitated indigotin was collected and washed with hot alcohol, dried, and crystallised from nitrobenzene:

0·1281 gave 0·0890 AgBr. Br = 29·6.

$C_{20}H_{16}O_6N_2Br_2$ requires Br = 29·6 per cent.

The substance is obtained in slender needles which have a particularly brilliant coppery lustre, and do not melt at 360°, but at about this temperature begin to carbonise. It is extremely sparingly soluble in solvents, and its dilute solutions in boiling nitrobenzene and aniline are pure blue.

The purple solution in sulphuric acid quickly becomes blue.

5-*Bromoveratraldehyde*.

This substance has been previously prepared by Dakin (*Amer. Chem. J.*, 1909, **42**, 494) by the methylation of 5-bromovanillin with methyl sulphate and potassium hydroxide, and also by Pschorr, Selle, Koch, Stoof, and Treidel (*Annalen*, 1912, **391**, 31) by a similar process applied to the product of bromination of protocatechualdehyde, but these authors give no details of the process employed. Our experiences in this connexion indicate a precaution which it is desirable to take in methylating phenolic aldehydes.

Vanillin was brominated in acetic acid by means of rather more than a molecular proportion of bromine, and the bromo-aldehyde was then methylated by methyl sulphate and potassium hydroxide in alcoholic solution. The operation was not entirely satisfactory owing to the readiness with which the aldehyde undergoes the Cannizzaro reaction, and no more than a 50 per cent. yield could be obtained. The conditions were similar to those which gave good results in the preparation of veratraldehyde (Perkin and Robinson, T., 1907, **91**, 1079), but for the reason mentioned the solution should never be allowed to become very strongly alkaline. On the addition of water, an oil separated, and usually slowly crystallised when the mixture was kept in a cold place. Occasionally, however, the oil could not be solidified, and was dissolved in ether and the aldehyde extracted by a solution of sodium hydrogen sulphite, from which it was regenerated as a readily crystallising oil by the addition of sodium carbonate. The substance was collected and dried and crystallised from light petroleum, from which it separated in felted needles melting at 62°.

On acidifying the alkaline solution from which the aldehyde was originally separated, a crystalline precipitate was obtained, and this was identified as 5-bromoveratric acid. The substance crystallised from water in needles melting at 191°, and the silver salt was prepared. (Found: Ag = 29·2. Calc.: Ag = 29·4 per cent.) The ethereal solution from which the aldehyde had been extracted by repeated washing with sodium hydrogen sulphite was dried and evaporated, and a yellow oil remained; this could not be crystallised, but was readily converted into a solid nitro-derivative by the action of nitric acid in acetic acid solution in the cold. The substance crystallised from alcohol in pale yellow, slender, brittle needles melting at 115°. This substance does not show the properties of a nitrobenzyl alcohol, and is unchanged after treatment with acetyl chloride or with benzoyl chloride in the presence of pyridine. On oxidation with potassium permanganate in alkaline solution, it yields the bromonitroveratric acid which is mentioned in the next section. It may be synthesised in the following manner. 5-Bromoveratraldehyde dissolved in a little alcohol was added to a concentrated solution of potassium hydroxide, and the mixture well shaken from time to time during three days. The bromohomoveratryl alcohol was extracted with ether, and any unchanged aldehyde removed by shaking the solution with aqueous sodium hydrogen sulphite. The extract was then dried and evaporated and the residue warmed with concentrated aqueous hydrobromic acid. On the addition of water, a crystal-

line substance was obtained, which was collected and thoroughly dried and then added to a solution of sodium methoxide in absolute methyl alcohol. Sodium bromide separated, and after gently warming on the steam-bath during fifteen minutes the addition of water precipitated an oil, which was isolated and nitrated, and so converted into the substance which is under discussion This result demonstrates that the nitro-derivative is 6-*bromo*-5-*nitro*-4-*methoxymethylveratrole*. Not only has the aldehyde been converted by the action of the alkali into the corresponding alcohol, but the latter has been transformed into its methyl ether by the action of the methyl sulphate.

5-*Bromoveratraldoxime*.—This derivative, obtained in the usual manner, crystallises from alcohol in needles melting at 85°.

5-*Bromo*-6-*nitroveratraldehyde;* 3-*Bromo*-4:5-*dinitroveratrole,*

$$\begin{array}{c}\text{MeO} \quad \text{CHO} \\ \text{MeO} \quad \text{NO}_2 \\ \text{Br}\end{array} ; \quad \begin{array}{c}\text{MeO} \quad \text{NO}_2 \\ \text{MeO} \quad \text{NO}_2 \\ \text{Br}\end{array}.$$
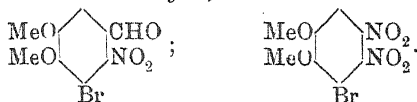
5-Bromoveratraldehyde was dissolved by very gently heating in ten times its weight of nitric acid (D 1·42), and the mixture allowed to remain overnight, when a considerable proportion of the nitro-derivative was found to have crystallised from the solution. Water was added, and the substance collected and crystallised from alcohol. There was no evidence of the formation of substances other than the nitro-aldehyde, and the colourless needles melted at 138°:

0·1310 gave 0·0850 AgBr. Br = 27·6.

$C_9H_8O_5NBr$ requires Br = 27·6 per cent.

The constitution of the substance was proved by oxidation to the corresponding acid and the transformation of this into a bromodinitroveratrole, which could be reduced to 4:5-diamino-veratrole. The aldehyde was finely powdered and suspended in N-potassium hydroxide, and then oxidised by potassium permanganate at 100° during half an hour. The permanganate was added gradually and so that there was always a moderate excess of the reagent. The oxidation of the aldehyde was found not to proceed in a satisfactory manner unless the solution was strongly alkaline, and this appears to be a general rule for such nitro-aldehydes, no doubt because the conversion to alcohol and acid assists the process. After the operation, the excess of oxidising agent was decomposed by alcohol and the yellow filtered solution acidified with hydrochloric acid. The colourless precipitate was

collected, and consisted of 5-*bromo*-6-*nitroveratric acid*, which is sparingly soluble in water and may be crystallised from dilute acetic acid, being obtained in colourless bunches of needles melting at 207°.

This acid, in view of its method of preparation, must be remarkably resistant towards potassium permanganate. It crystallised unchanged from nitric acid (D 1·4), but when boiled with an excess of fuming nitric acid (D 1·52) was transformed into 3-*bromo*-4:5-*dinitroveratrole* by elimination of the carboxyl group. The product was washed with dilute aqueous potassium hydroxide and crystallised from alcohol, being obtained in pale yellow needles melting at 121°:

0·1149 gave 0·0712 AgBr.   Br = 26·4.

$C_8H_7O_6N_2Br$ requires Br = 26·1 per cent.

This substance was also obtained by the action of fuming nitric acid on 6-bromo-5-nitroveratrole. Vigorous reduction removed the bromine atom, and in order to ensure the completion of the reaction the following method was used. The bromodinitroveratrole (1 gram), dissolved in hot alcohol (30 c.c.), was mixed with hydrochloric acid (5 c.c.) and zinc dust (10 grams) added in one portion. The stormy reaction over, water was added, and the mixture boiled during four hours. The solution was filtered, mixed with an excess of sodium acetate and with a solution of phenanthraquinone (1·5 grams) in aqueous sodium hydrogen sulphite, and heated to boiling. The precipitated phenazine derivative was crystallised from acetic acid and then thrice from xylene, and obtained in slender, yellow needles melting at 260°, which were identified with 2:3-dimethoxyphenanthraphenazine (Moureu, *Compt. rend.*, 1896, **123**, 33).

7 : 7′-*Dibromo*-5 : 6 : 5′ : 6′-*tetramethoxyindigotin*,
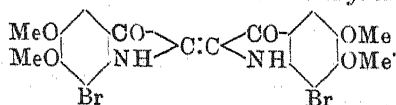
This substance was obtained from 5-bromo-6-nitroveratraldehyde by the employment of a method precisely identical with that described above for an isomeride. The indigotin derivative was produced in good yield, and was crystallised from nitrobenzene, in which, as in all other solvents, it is very sparingly soluble, and obtained in deep blue needles which have a bronze glance, but not a particularly striking one. The substance does not melt or appear to decompose at 360°:

0·1463 gave 0·1022 AgBr.   Br = 29·7.

$C_{20}H_{16}O_6N_2Br$ requires Br = 29·6 per cent.

The solution in sulphuric acid is intense royal-blue and does not change on keeping.

6-*Nitroveratryl*-4 : 5-*thiotriazoveratrole* (XI).

4 : 5-Dinitroveratrole (9 grams) was dissolved in hot alcohol (300 c.c.), mixed with aqueous ammonia (50 c.c., D 0·88), and the liquid rapidly saturated with hydrogen sulphide. In a few minutes a crystalline precipitate separated, and was collected and crystallised by adding alcohol to its solution in nitrobenzene, and then several times from xylene:

0·1174 gave 0·2122 CO_2 and 0·0433 H_2O.   C = 49·3 ; H = 4·1.

0·1260   ,,   15·4 c.c. N_2 at 19° and 763 mm.   N = 14·4.

0·1243   ,,   0·0712 $BaSO_4$.   S = 7·9.

$C_{16}H_{16}O_6N_4S$ requires C = 49·0 ; H = 4·1 ; N = 14·3 ; S = 8·2 per cent.

The orange, lanceolate prisms melt at 219°, and this substance is very sparingly soluble in most organic solvents. It dissolves in sulphuric acid to a Bordeaux-red solution, and on the addition of water is precipitated unchanged; in this and other respects it fails to exhibit any basic properties.

6-*Aminoveratryl*-4 : 5-*thiotriazoveratrole*.

The nitro-derivative (10 grams), mixed with hydrochloric acid (50 c.c.) and acetic acid (10 c.c.), was heated on the steam-bath with an excess of granulated tin until all the orange compound had entered into reaction and its place was taken by a colourless, crystalline precipitate of the hydrochloride of the new base. Since the separation of this salt appeared to be quantitative, it was collected, dissolved in water, and decomposed by the addition of potassium hydroxide. The base was several times recrystallised from alcohol and from toluene, and obtained in characteristic stellar aggregates of colourless leaflets with a satiny appearance, melting at 114°:

0·1165 gave 0·2272 CO_2 and 0·0558 H_2O.   C = 53·2 ; H = 5·3.

0·1317   ,,   17·4 c.c. N_2 at 16° and 762 mm.   N = 15·7.

0·1490   ,,   0·1006 $BaSO_4$.   S = 9·2.

$C_{16}H_{18}O_4N_4S$ requires C = 53·0 ; H = 5·0 ; N = 15·5 ; S = 8·9 per cent.

The pure substance dissolves in sulphuric acid to a colourless solution, but the crude material contains an impurity which develops a rose colour under these conditions, and this becomes deep blue, and finally violet, on the addition of water. The salts of the base are rather sparingly soluble, and the hydrochloride

crystallises from hot water in slender, colourless needles, and on the addition of ferric chloride to its dilute aqueous solution, a splendid deep blue coloration slowly appears.   This reaction is characteristic of many veratrylamine derivatives, and is the result of oxidation, which in the case of homoveratrylamine was shown (Luff, Perkin, and Robinson, T., 1910, **97**, 1137) to lead to the production of a *p*-quinone by elimination of the amino- and methoxy-groups.   There was evidence that the reaction proceeded in a similar direction in the present instance, but the quinone could not be isolated in a pure condition.

The base is diazotisable, and the azo-β-naphthol derivative is intense crimson and was obtained in part in a colloidal condition, so that even a filtered solution appeared to have violet fluorescence, due, however, to suspended particles.   The acetyl derivative of the base could not be obtained in a crystalline condition.   It is produced on warming the amine with acetic anhydride, and, after the addition of water, a clear solution is obtained from which the acetylamino-compound is precipitated only by the addition of alkali.   It is not diazotisable and gives no colour with ferric chloride, so that, the acetylation being complete, it is evident that basic function can in some circumstances be exercised by the heterocyclic nucleus contained in these curious substances.

5(or 6)-*Nitro*-6(or 5)-*amino*-1:2:4-*trimethoxybenzene*,

<div style="text-align:center">

NH₂   NO₂

MeO⟨ ⟩NO₂   or   MeO⟨ ⟩NH₂ .
MeO⟨ ⟩OMe   MeO⟨ ⟩OMe

</div>
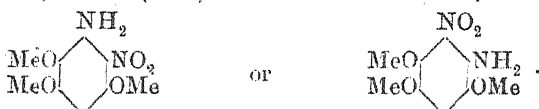
The behaviour of dinitroveratrole on reduction with ammonia and hydrogen sulphide induced us to investigate other cases of a similar character, and having in our possession a specimen of 5:6-dinitro-1:2:4-trimethoxybenzene (Blanksma, *Chem. Weekblad*, 1912, **9**, 440), we applied the reaction to this substance and obtained as sole product a nitroamine.   A mixture of 5:6-dinitro-1:2:4-trimethoxybenzene (7 grams), ethyl alcohol (100 c.c.), and aqueous ammonia (80 c.c., D 0·88) was saturated in the cold with hydrogen sulphide and then boiled under reflux during half an hour.   The liquid was diluted with water and allowed to remain in the ice-chest, when long yellow needles gradually separated, and were collected and crystallised from water and then from a mixture of benzene and light petroleum (b. p. 50—60°).   The substance crystallises in bright orange-yellow needles or in well-defined orange prisms melting at 118°:

0·1146 gave 0·1986 CO_2 and 0·0538 H_2O. C = 47·3; H = 5·2.

$C_9H_{12}O_5N_2$ requires C = 47·4; H = 5·2 per cent.

The melting point of this substance was quite sharp and the appearance of the crystals did not vary, so that it seems that only one of the two possible nitroamines was actually obtained. The base dissolves in concentrated hydrochloric acid, but a pale yellow hydrochloride soon separates in prisms. On the addition of water the salt is decomposed and the orange base precipitated, and on the further addition of a solution of sodium nitrite a clear yellow solution of a diazonium salt is produced. The latter gives with excess of sodium acetate and β-naphthol a scarlet azo-compound dissolving in sulphuric acid to an intense blue solution, which becomes crimson on the addition of water.

1 : 2-*Methylenedioxyphenanthraphenazine,*
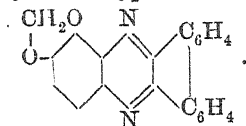
4-Bromo-5 : 6-dinitrocatechol methylene ether (4 grams) and tin (5 grams) were mixed with a solution of stannous chloride (10 grams) in concentrated hydrochloric acid (15 c.c.) and acetic acid (10 c.c.), and shaken in a bottle at the ordinary temperature until the solid nitro-compound had disappeared. The solution was diluted and the tin eliminated as sulphide, and, after boiling the filtered liquid, excess of sodium acetate and then a solution of phenanthraquinone (3 grams) in hot aqueous sodium hydrogen sulphite was added. The mixture was boiled during three minutes, and the yellow precipitate was collected, washed with boiling water, and dried. It was then dissolved in boiling acetic acid and the solution distilled until crystallisation commenced; the material so obtained had a bronze lustre in mass, but under the microscope was seen to consist of transparent, yellow, elongated, rectangular prisms. For analysis, the substance was recrystallised from toluene and obtained as a copper-bronze powder consisting of leaf-shaped crystals. It melts at 307—309° and is very sparingly soluble in most organic solvents:

0·1282 gave 0·3648 CO_2 and 0·0448 H_2O. C = 77·6; H = 3·9.

$C_{21}H_{12}O_2N_2$ requires C = 77·7; H = 3·7 per cent.

The substance dissolves in sulphuric acid to a rose-red solution, but is especially characterised by the intense green fluorescence exhibited by its yellow solutions in neutral organic solvents. The

isomeric 2 : 3-methylenedioxyphenanthraphenazine gives very pale yellow solutions which exhibit violet fluorescence.

4-Bromo-1 : 2-dimethoxyphenanthraphenazine,
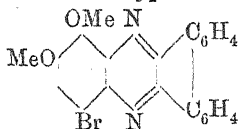
4-Bromo-5 : 6-dinitroveratrole was treated exactly as described for the methylenedioxy-derivative in the last section, but the precipitated phenazine was in this case crystallised from xylene. Bright yellow clusters of needles melting at 206—208° were obtained, and the same substance was produced by the bromination of 1 : 2-dimethoxyphenanthraphenazine in acetic acid solution and suspension :

0·1083 gave 0·0493 AgBr. Br = 19·4.

$C_{22}H_{15}O_2N_2Br$ requires Br = 19·1 per cent.

The solution in sulphuric acid is reddish-purple, and in benzene or alcohol yellow with weak green fluorescence.

1 : 2 : 4-Trimethoxyphenanthraphenazine,
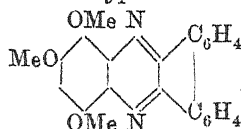
The nitro-aniline (0·5 gram), obtained as described above by the reduction of 5 : 6-dinitro-1 : 2 : 4-trimethoxybenzene, was dissolved in hot alcohol (10 c.c.), mixed with concentrated hydrochloric acid (3 c.c.), and zinc dust added until the solution was quite colourless. After diluting with water, the filtered liquid was saturated with sodium acetate and mixed with a solution of phenanthraquinone (1 gram) in aqueous sodium hydrogen sulphite. The mixture was boiled during five minutes, and the precipitated phenazine derivative was then collected and crystallised from alcohol, from which it separated in bright yellow, felted needles melting at 186° :

0·0992 gave 0·2729 CO_2 and 0·0449 H_2O. C = 75·0 ; H = 5·0.

$C_{23}H_{18}O_3N_2$ requires C = 74·6 ; H = 4·9 per cent.

The substance is sparingly soluble and its dilute solutions do not exhibit visible fluorescence. The solution in sulphuric acid is magenta, and becomes brownish-green on dilution with water.

1 : 2 : 3 :-*Trimethoxyphenanthraphenazine,*
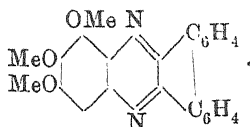
Dinitropyrogallol trimethyl ether (Will, *Ber.*, 1888, **21**, 612) was converted into a phenanthraphenazine derivative by reduction with zinc and hydrochloric acid in alcoholic solution, followed by condensation with phenanthraquinone, dissolved in sodium hydrogen sulphite solution, in the presence of excess of sodium acetate. The substance was crystallised from acetone and obtained in pale yellow needles melting at 180°:

0·1133 gave 0·3110 CO_2 and 0·0487 H_2O. C = 74·8; H = 4·8.
$C_{23}H_{18}O_3N_2$ requires C = 74·6; H = 4·9 per cent.

The solution in sulphuric acid is intense reddish-purple, and on the addition of water becomes reddish-brown. Much water precipitates a red substance, and the solution becomes colourless. Dilute solutions in benzene or alcohol are non-fluorescent. The substance is quite distinct from the 1 : 2 : 4-trimethoxyphenanthraphenazine described above.

UNIVERSITY OF SYDNEY.   [*Received, September 4th,* 1917.]

LXXVIII.—*The Scission of Certain Substituted Cyclic Catechol Ethers.*

By GERTRUDE MAUD ROBINSON and ROBERT ROBINSON.

IT was observed (G. M. Robinson, this vol., p. 113) that, on attempting to produce an azoxy-derivative from 4-nitrocatechol methylene ether (4-nitromethylenedioxybenzene) (I) by the action of sodium methoxide in methyl-alcoholic solution, the sole product was a nitrophenol, although the corresponding reaction with nitro-veratrole proceeds smoothly in the normal manner. On further investigation, the nitrophenol was readily identified as 5-nitro-guaiacol (II), and the process appeared at first sight to be one of reduction. However, an alternative view suggested itself, namely, that the methoxy-group was derived from the methyl alcohol used as solvent, and this was proved to be the case, since, when ethyl

alcohol was used, a quantitative yield of 5-nitro-2-ethoxyphenol (III) was obtained.

(I.)   (II.)   (III.)
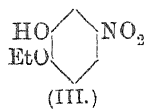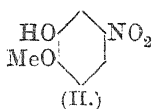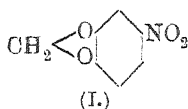
The mechanism of the reaction is therefore to be represented in the following manner:
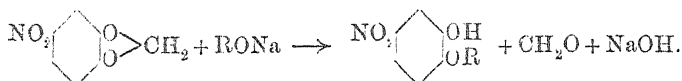
Blanksma (*Chem. Weekblad*, 1909, **6**, 313) has demonstrated the reversible interchange of alkyloxyl groups in nitro-, and especially dinitro-, phenol ethers, and, for example, 2:4-dinitro-anisole is changed in ethyl-alcoholic solution in the presence of traces of alkali into 2:4-dinitrophenetole; but in the majority of instances mononitrophenol ethers are unchanged under these conditions. In the case of nitrocatechol methylene ether, the greater reactivity may be due to the influence of the oxygen atom in the meta-position with respect to the nitro-group on the distribution of affinity, and this is confirmed by the observation that we find it impossible to realise a similar reaction in the case of nitroethylene-dioxybenzene (IV), in which substance the oxygen atom is one atom further removed from the point of attack. Cardwell and Robinson (T., 1915, **107**, 255) showed that 5-nitroguaiacol is obtained by the hydrolysis of nitroveratrole with hydrobromic acid, and that its acetyl derivative results when acetylguaiacol is nitrated. Similarly, the hydrolysis of nitrocatechol diethyl ether with hydrobromic acid is now found to yield 5-nitro-2-ethoxy-phenol, and the benzoyl derivative (V) of this substance is obtained by the nitration of 2-benzo-, —ietole.

(IV).   (V.)   (VI.)
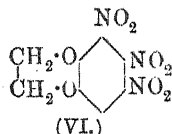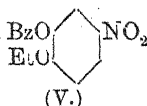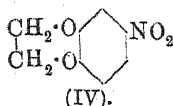
In order to examine the scission of the ethylenedioxy-ring, we submitted 4:5:6-trinitroethylenedioxybenzene (VI) to the action of ammonia. It was quickly changed to a mixture of 3:5-dinitro-2:4-diamino-β-hydroxyethoxybenzene (VII) and 4:5-dinitro-6-aminoethylenedioxybenzene (VIII). The benzoyl derivative (IX) of the former substance exists in two highly characteristic chromo-

isomeric modifications, which are described in the experimental portion on p. 938.

(VII.)   (VIII.)   (IX).
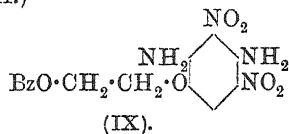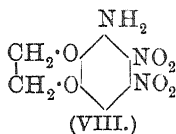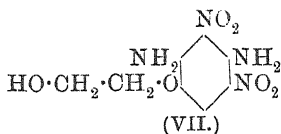
The substance VII is rapidly and quantitatively hydrolysed by hot aqueous alkali hydroxides, with the production of two molecules of ammonia and the phenol X, which was transformed into the well-known dinitrodiaminoanisole (XI), as shown below.

(X.)   (XI.)
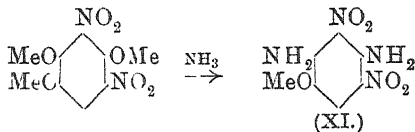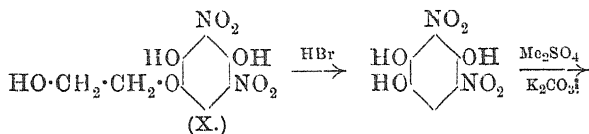
In view of the close analogy which exists between the hydroxyl of the carboxyl group and the hydroxyl of *op*-dinitrophenols, it is interesting to note that the substance X shows no tendency to form an internal anhydride. It would be fair to conclude from this that lactone-formation in some way involves the whole carboxyl group, and not merely the acidic hydroxyl of that group. In the nitrophenols it is the whole conjugated system extending from the nitro-group to the hydroxyl that corresponds with the carbonyl in the acids, and the steric conditions favourable to lactone-formation are accordingly not necessarily present in the dinitrophenol (X).

The constitution of the dinitroamine VIII was proved by eliminating the amino-group, when 4:5-dinitroethylenedioxybenzene was obtained. The nitro-groups in positions 4 and 5 in trinitroveratrole have previously been shown to be displaceable under certain conditions, but this is the first example of the displacement of the 6-nitro-group in a trinitrocatechol ether. We are inclined to assign the result to the unexplained influence which a fused ring has on the α-position in rendering atoms and groups

attached at this point more liable to substitution and displacement. Naphthalene, for example, yields α-nitronaphthalene on nitration, and the reactivity of groups in the 1-, 4-, 5-, or 8-positions in substituted anthraquinones may also be cited.

EXPERIMENTAL.

Preparation of 4-Nitrocatechol Methylene Ether.

Salway has shown (T., 1908, **95**, 1163) that the nitration of piperonal yields nitrocatechol methylene ether in addition to nitropiperonal, and when the former substance is the object of preparation, the nitroaldehyde may be converted, as described in the foregoing communication, into 5-nitro-4-aminocatechol methylene ether (compare p. 915), from which the amino-group may be eliminated in the usual manner. 5-Nitro-4-aminocatechol methylene ether (9 grams) was mixed with alcohol (150 c.c.), sulphuric acid (15 c.c.), and powdered sodium nitrite (5 grams), and the solution boiled during five minutes, after which a further quantity of sodium nitrite (4 grams) was added and the heating continued for five minutes longer. The crystalline precipitate obtained after the addition of water was collected and dried, and weighed 8 grams. After crystallisation from alcohol the substance melted at 147°, and at the same temperature, when mixed with a specimen of 4-nitrocatechol methylene ether obtained by the nitration of piperonal.

Formation of 5-Nitroguaiacol by the Interaction of Nitrocatechol Methylene Ether and Sodium Methoxide.

Nitrocatechol methylene ether (1·1 grams) was heated on the steam-bath with a solution of sodium methoxide (from 3 grams of sodium and 40 grams of methyl alcohol) until the red sodium salt of the nitrophenol crystallised from the solution. This requires from one to three minutes. After cooling, the salt was separated, washed with ether, dissolved in water, and the solution acidified with hydrochloric acid. The yellow precipitate was collected (1·0 gram when dry) and recrystallised from water, when it was obtained in needles melting at 105°, and at the same temperature when mixed with 5-nitroguaiacol.

5-Nitro-2-ethoxyphenol (III).

An almost quantitative yield of this substance was produced when nitrocatechol methylene ether was treated in ethyl-alcoholic solution with sodium ethoxide under precisely the same conditions

as are described above for the corresponding reaction with sodium methoxide. In this case no salt separated from the solution, but the reaction was as rapid as in the former example. The substance is more sparingly soluble in water and alcohols than is 5-nitroguaiacol, and separates from methyl alcohol containing a little water in pale yellow, well-defined prisms melting at 113—114°:

0·1478 gave 0·2854 CO_2 and 0·0671 H_2O.   C = 52·7; H = 5·0.
$C_8H_9O_4N$ requires C = 52·5; H = 4·9 per cent.

The substance dissolves in sodium carbonate solution, and the orange-red colour produced can scarcely be distinguished from that of a similar solution of 5-nitroguaiacol. In view of the fact that 4-nitroguaiacol dissolves in sodium carbonate to a yellow solution, this behaviour indicates the constitution of the substance, and the matter is placed beyond doubt by the preparation of 5-nitro-2-ethoxyphenol by the two following methods, which in the corresponding methoxy-series lead to 5-nitroguaiacol.

(A) 2-Ethoxyphenol was benzoylated by an application of the Schotten-Baumann reaction, and the dry benzoyl derivative dissolved in an excess of cold nitric acid (D 1·42). Undue rise of temperature was checked, and, after ten minutes, the clear solution was added to water and the precipitated oil induced to solidify by the usual methods. The solid was collected and crystallised from methyl alcohol, when it was obtained in felted masses of slender, colourless needles melting at 101—102°:

0·1108 gave 4·7 c.c. N_2 at 18° and 762 mm.   N = 5·0.
$C_{15}H_{13}O_5N$ requires N = 4·9 per cent.

5-*Nitro-2-ethoxyphenyl benzoate* was dissolved in boiling ethyl alcohol and hydrolysed by the addition of a solution of three times its weight of potassium hydroxide dissolved in water. After heating on the steam-bath during three minutes, it was found that a sample was completely soluble in water. Excess of alcohol was removed, the residue dissolved in water, just acidified with hydrochloric acid, and then treated with sufficient aqueous sodium carbonate to restore a faint orange colour to the liquid. Under these conditions, the benzoic acid remained in solution and the nitrophenol was precipitated. It was collected, crystallised from aqueous methyl alcohol, and melted at 112—114°, and at the same temperature when mixed with some of the substance prepared from nitrocatechol methylene ether.

(B) 4-Nitrocatechol diethyl ether * (20 grams) was heated on

* 4 : 5-*Dinitrocatechol diethyl ether*, $C_{10}H_{12}O_6N_2$, does not appear to have been previously prepared. It was obtained in quantitative yield by dissolving the mononitro-derivative in nitric acid (D 1·42). In about half an

the steam-bath during three hours with a saturated solution (80 grams) of hydrobromic acid in acetic acid. After the addition of water, the solution was rendered alkaline by the addition of sodium hydroxide, and the unchanged substance removed by filtration (3 grams). The filtrate was acidified and the precipitated mixture of nitrophenols collected (14 grams). After several crystallisations from aqueous methyl alcohol, 8 grams of pure 5-nitro-2-ethoxyphenol melting at 112—114° were obtained. The melting point was not depressed by admixture with a specimen of the substance obtained by the method (*A*) described above. The alcoholic mother liquors were added to the aqueous solution from which the crude phenol was separated, and the whole was extracted with ether. The recovered mixed nitrophenols were converted into benzoyl derivatives by treatment with benzoyl chloride and sodium hydroxide in aqueous solution, and the mixture of the benzoates was then fractionally crystallised from methyl alcohol. The most sparingly soluble substance crystallised in slender needles, and was recrystallised from acetic acid. It melted at 156°, and was identified as the *dibenzoyl* derivative of *nitrocatechol*. The substance was also obtained in the following manner: *o*-Phenylene benzoate (13 grams) was added to cold nitric acid (50 c.c., D 1·42), when the benzoate became an oil which was well mixed with the acid. After remaining overnight, the nitration was completed and

hour the dinitro-derivative began to separate from the solution, which was gently warmed to ensure the completion of the reaction. Water was added and the solid collected and crystallised from alcohol, from which it separated in characteristic citron-yellow, micaceous flakes melting at 113° and rather sparingly soluble in alcohol. It is quantitatively converted by nitric acid in sulphuric acid solution to the 4:5:6-trinitrocatechol diethyl ether which Blanksma (*Rec. trav. chim.*, 1905, **24**, 40) has obtained by the nitration of 4:6-dinitrocatechol diethyl ether. The substance melted at 122° and was converted by alcoholic ammonia into 3:5-*dinitro*-2:4-*diaminophenetole*, crystallising from nitrobenzene in hæmatite-like plates melting at 257° (Nietzki; *Annalen*, 1882, **215**, 153, and Blanksma, *loc. cit.*, give 245°).

0·4951 distilled with 10 per cent. aqueous potassium hydroxide evolved NH₃, which neutralised 40·8 c.c. *N*/10-HCl, whereas this amount of a substance, $C_8H_{10}O_5N_4$, yielding 2NH₃ requires 40·9 c.c.

4:5-Dinitrocatechol diethyl ether dissolved in hot aqueous alcoholic hydrochloric acid was reduced by the addition of zinc dust. The colourless solution was mixed with sodium acetate and filtered. The filtrate was then heated with a solution of phenanthraquinone in hot sodium hydrogen sulphite solution and a voluminous pale yellow precipitate of the phenazine derivative was quickly formed. The substance was collected and crystallised from xylene. 2:3-*Diethoxyphenanthraphenazine*, $C_{24}H_{20}O_2N_2$, crystallises in pale flesh-coloured needles which change on keeping in contact with the solvent into rectangular plates melting at 230°. It dissolves in sulphuric acid to a bright magenta solution, yellow on dilution with water, and in benzene to a pale yellow solution which exhibits intense violet fluorescence.

the derivative had solidified.   Water was added, and the substance collected and crystallised from acetic acid and acetone.   The substance melted at 156°, and at the same temperature when mixed with the product obtained as above:

0·2091 gave 6·4 c.c. N_2 at 17° and 756 mm.   N = 3·6.

$C_{20}H_{13}O_6N$ requires N = 3·9 per cent.

After the separation of the relatively small quantity of the dibenzoate, a substance crystallised in colourless prisms which is undoubtedly the *benzoyl* derivative of *4-nitro-2-ethoxyphenol*.   It could not be obtained in a pure condition, and always melted over a considerable range of temperature.   A few crystals were mechanically separated, and it was noted that on hydrolysis a nitrophenol was obtained which gave a pure yellow solution in aqueous alkali, whereas nitrocatechol gives a blood-red and 5-nitro-2-ethoxyphenol an orange-red solution.   From the mother liquors, considerable quantities of the benzoyl derivative of 5-nitro-2-ethoxyphenol melting at 101° were obtained.

4 : 5 : 6-*Trinitroethylenedioxybenzene* (VI).

The ethylene ether of nitrocatechol is less readily nitrated than the corresponding dimethyl or diethyl ethers, and it was found desirable to operate under the following conditions, which are more convenient than those employed by Ghosh (T., 1915, **107**, 1591) for the same purpose:

4-Nitroethylenedioxybenzene (10 grams) was dissolved in nitric acid (100 grams, D 1·5), and, after remaining overnight at the ordinary temperature, water was added and the precipitate collected and crystallised from alcohol.   The substance was obtained in prismatic needles melting at 132—133°, and was occasionally also obtained in leaflets melting at the same temperature.   It separated from acetic acid in plates.   The substance is readily reduced to a diamine which gives a red coloration with ferric chloride and condenses with phenanthraquinone to the sparingly soluble 2 : 3-*ethylenedioxyphenanthraphenazine*,

$$C_{22}H_{14}O_2N_2,$$

which crystallises from acetic acid in clusters of slender, yellow needles melting at 239—240°.   The colour reaction in sulphuric acid and the fluorescence in benzene are indistinguishable from those exhibited by 2 : 3-dimethoxyphenanthraphenazine.

4 : 5-Dinitroethylenedioxybenzene (22 grams) was finely powdered and dissolved as far as possible in sulphuric acid (100 c.c.), and gradually nitrated by the addition, with cooling, of nitric acid (20 c.c., D 1·5) in sulphuric acid (20 c.c.).   The dinitro-compound

passed into solution and the trinitro-derivative crystallised out. The mixture was poured into water, and the colourless solid collected and crystallised from alcohol. The substance was sparingly soluble, and separated in laminæ melting at 155—156°, as stated by Ghosh (*loc. cit.*). From concentrated solutions it was obtained in prismatic needles:

0·1169 gave 0·1509 CO_2 and 0·0141 H_2O.   C = 35·2; H = 1·4.
    $C_8H_5O_8N_3$ requires C = 35·4; H = 1·8 per cent.

Each stage in the nitration of ethylenedioxybenzene proceeds in a quantitative manner.

3 : 5-*Dinitro-2 : 4-diamino-β-hydroxyethoxybenzene* (VII).

This substance is obtained by the action of ammonia on trinitroethylenedioxybenzene, but when the reaction was carried out in ethyl-alcoholic solution it was found that the percentage of carbon obtained on analysis was consistently about 1 per cent. too high, and the amount of ammonia obtained on hydrolysis with aqueous potassium hydroxide was also greater than the theoretical. This indicated that a diamino-derivative of similar constitution and properties, but of smaller molecular weight, contaminated the product, and eventually proof was obtained that the impurity was dinitrodiaminophenetole. The production of this substance clearly showed that the trinitroethylenedioxybenzene, under the influence of the alcoholic ammonia, was converted in part into trinitrocatechol diethyl ether, and accordingly the use of alcohol as a solvent was avoided. The following conditions were ultimately adopted: Trinitroethylenedioxybenzene (12 grams) was dissolved in pyridine (50 grams) and heated on the steam-bath under reflux with aqueous ammonia (50 c.c., D 0·880). In a short time the product of the reaction separated in red needles, and a further quantity of ammonia solution (50 c.c.) was then added and the heating continued for half an hour. After cooling and adding water, the orange-red solid was collected, and when dry weighed 9·5 grams. This material is a mixture containing about 75 per cent. of dinitrodiaminohydroxyethoxybenzene and about 25 per cent. of a dinitroaminoethylenedioxybenzene. The two substances may be approximately separated by crystallisation from xylene, in which the former is the more sparingly soluble. The further purification of the second crop of crystals is described below, but the intense red crystals which separate first can be obtained in a pure condition by two recrystallisations from nitrobenzene. It is perhaps better to extract the crude product with hot xylene insufficient to dissolve the whole, and then to crystal-

lise the residue from nitrobenzene.   The substance occurs in deep red needles melting at 240°:

0·1543 gave 0·2127 CO_2 and 0·0583 H_2O.   C = 37·6; H = 4·2.

0·0978   ,,   18·2 c.c. N_2 at 24° and 750 mm.   N = 21·1.

$C_8H_{10}O_6N_4$ requires C = 37·2; H = 3·9; N = 21·7 per cent.

0·3977 distilled with 50 c.c. of 10 per cent. aqueous potassium hydroxide evolved NH_3, which neutralised 31·0 c.c. $N/10$-HCl, whereas this amount of a substance, $C_8H_{10}O_6N_4$, yielding $2NH_3$, requires 30·8 c.c.

This substance resembles in its behaviour the similarly constituted dinitrodiaminophenetole.   It is quite devoid of basic character and is very sparingly soluble in organic solvents.   When its solution in sulphuric acid is treated with sodium nitrite, a reaction of unexplained character occurs, and on the addition of water there is produced a transient, intense purple coloration. This quickly disappears, and the yellow solution contains traces of some diazo-salt, as indicated by coupling with "R-salt," but the major part of the substance has undergone decomposition.

3 : 5-*Dinitro*-2 : 4-*diamino*-β-*benzoyloxyethoxybenzene* (IX).

It was noticed that the amino-groups of dinitrodiaminoanisole and the corresponding phenetole derivative cannot be benzoylated by the action of pyridine and benzoyl chloride on these substances. Recourse was therefore had to this reaction in order to prove the presence of a hydroxyl group in the substance described in the last section.   The dinitrodiaminohydroxyethoxybenzene (4 grams) was dissolved in pyridine (30 c.c.) and benzoyl chloride (15 c.c.). A certain amount of heat was developed, and, when the reaction had subsided, ether was added and the red precipitate collected and washed with water.   It was dried in the air and then crystallised from ethyl acetate, in which it is sparingly soluble:

0·1526 gave 0·2800 CO_2 and 0·0560 H_2O.   C = 50·0; H = 4·1.

$C_{15}H_{14}O_7N_4$ requires C = 49·7; H = 3·9 per cent.

0·3827 distilled with aqueous potassium hydroxide evolved NH_3, which neutralised 21·5 c.c. $N/10$-HCl, whereas this amount of a substance, $C_{15}H_{14}O_7N_4$, yielding $2NH_3$, requires 21·2 c.c.

On acidifying the alkaline solution from this experiment, benzoic acid and 3 : 5-dinitro-2 : 4-dihydroxy-β-hydroxyethoxybenzene (X) were obtained as a crystalline precipitate.   The latter substance was identified after removal of the benzoic acid by repeated evaporations of the solution in water.

This benzoyl derivative is dimorphous and occurs in two distinct chromoisomeric modifications.   Both forms melt at 180—181°

alone or mixed. The crimson form crystallises readily from most solvents, and may be easily obtained by crystallisation from xylene or by the addition of ether, alcohol, or light petroleum to a solution of the substance in pyridine. It occurs in crimson plates with parallel edges. The orange-yellow modification is characterised by its sparing solubility in ethyl acetate, and is the first to crystallise from this solvent. It is obtained by heating the red form or a mixture of the two to near the melting point, and then extracting the material with ethyl acetate. It crystallises from this solvent in needles. The change from red to yellow on heating also occurs slowly at temperatures above 100°, but nothing in the nature of a transition point could be determined. Recrystallisation of either form from nitrobenzene resulted in crimson leaflets containing solvent of crystallisation.

$3:5$-*Dinitro-2 : 4-dihydroxy-β-hydroxyethoxybenzene* (X).

This substance was readily obtained by boiling dinitrodiamino-β-hydroxyethoxybenzene with a 10 per cent. solution of potassium hydroxide until all the ammonia was evolved. The reaction was complete in a few minutes, and the orange solution was acidified with hydrochloric acid. Bronze-yellow needles separated on cooling, and the substance was purified by recrystallisation from dilute hydrochloric acid. It is readily soluble in water or alcohol, less readily so in dilute hydrochloric acid, and it has powerful dyeing properties. The substance forms well-defined, brittle needles which darken at 160° and melt and decompose at 170°:

0·1379 gave 0·1884 CO_2 and 0·0395 H_2O.   C = 37·3; H = 3·2.
$C_8H_8O_8N_2$ requires C = 36·9; H = 3·1 per cent.

This compound shows no tendency to change by loss of water to a lactone-like ethylenedioxy-derivative. Its constitution was proved in the following manner: The glycol residue was removed by boiling several hours with an excess of concentrated hydrobromic acid, and the resulting phenol converted into its trimethyl ether by means of methyl sulphate and potassium carbonate in boiling nitrobenzene solution. This substance was then heated at 100° in a sealed tube with concentrated aqueous ammonia, and the resulting red precipitate crystallised from nitrobenzene. The red plates were identified as consisting of $3:5$-dinitro-2:4-diaminoanisole, and melted at 255°, and at the same temperature when mixed with a specimen of the substance obtained from trinitroveratrole.

4 : 5-Dinitro-6-aminoethylenedioxybenzene (VIII).

This by-product of the preparation of dinitrodiaminohydroxy-ethoxybenzene from trinitroethylenedioxybenzene is separated in an impure form by extracting the crude product with xylene as already described. It may be freed from its congener by taking advantage of the ready attack of the latter by warm aqueous potassium hydroxide. The crude crystals obtained from xylene were carefully warmed with a 5 per cent. solution of potassium hydroxide until the precipitate had a pure yellow colour. The substance was then collected, washed with water, and several times crystallised from ethyl acetate, from which it separated in orange-yellow, rhombic prisms melting at 202°:

0·1133 gave 0·1676 CO_2 and 0·0340 H_2O.   C$=40·2$; H$=3·3$.
$C_8H_7O_6N_3$ requires C$=39·8$; H$=2·9$ per cent.

The substance is sparingly soluble in most solvents and has weak basic character. On boiling with aqueous potassium hydroxide, it is slowly attacked, yielding a cherry-red solution. The base is diazotisable in dilute hydrochloric acid suspension, and the diazonium salt couples with β-naphthol to a crimson azo-compound. When trinitroethylenedioxybenzene is reduced in alcoholic hydrochloric acid with zinc dust, a colourless solution is obtained which gives an intense green coloration with ferric chloride. The substance now under consideration shows the same behaviour. On boiling with alcoholic sulphuric acid and powdered sodium nitrite, the amino-group was easily removed, and, after the addition of water, pearly leaflets separated and were collected. The substance was recrystallised from alcohol, and melted at 132—133° alone or mixed with a specimen of 4 : 5-dinitroethylenedioxybenzene. Since the constitution of the latter substance is known by inference only, the material obtained from the above experiment was hydrolysed by heating with concentrated aqueous hydrobromic acid, and the dinitrocatechol so obtained methylated in the usual manner and the product identified with 4 : 5-dinitroveratrole.

Acetyl Derivative.—The dinitroamine could be recrystallised from acetic anhydride, but on the addition of a trace of sulphuric acid the amino-group was acetylated, and the derivative was collected after decomposition of the excess of acetic anhydride by means of dilute hydrochloric acid. The substance was recrystallised from alcohol, in which it is sparingly soluble, and obtained in hexagonal prisms melting at 257°. The substance appears colourless when first prepared, but the compact crystals have a pale yellow colour.

The similarly constituted 4 : 5-dinitro-3-acetylaminoveratrole has recently been prepared by Gibson, Simonsen, and Rau (this vol., p. 78), who find that it dissolves in aqueous potassium hydroxide to a yellow solution which on acidification gives a precipitate of the unchanged substance. This ethylene ether shows the same characteristic behaviour.

LXXIX.—5-*Bromoguaiacol and some Derivatives.*

By ELLEN MARGARET HINDMARSH, ISABEL KNIGHT, and ROBERT ROBINSON.

IN the course of the investigation described in the preceding communication it was found that 5-nitroguaiacol yielded on bromination an ortho- and not, as would have been anticipated, a para-bromophenol, and it was therefore desired to prepare other guaiacol derivatives substituted in the 5-position in order to examine their behaviour on bromination.

Cardwell and Robinson (T., 1915, **107**, 255) have already shown that the methoxy-group of acetylguaiacol has a far greater orientating effect than the acetoxy-group, and accordingly the bromination of acyl derivatives of guaiacol leads to the corresponding derivatives of 5-bromoguaiacol (I). This phenol behaves normally on further bromination and yields 4 : 5-dibromoguaiacol (II).

(I.)   (II.)   (III.)   (IV.)
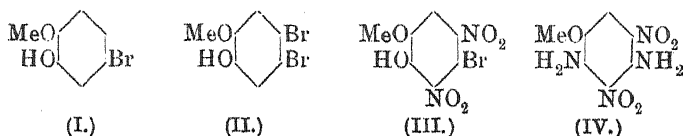
A mononitro-derivative of the bromoguaiacol could not be isolated, and the constitution of the substance is indicated by the fact that the reaction with nitric acid leads to bromodinitroguaiacol (III), and proved by the conversion of the methyl ether of the latter by alcoholic ammonia into 3 : 5-dinitro-2 : 4-diaminoanisole (IV). The methyl ether of III has a curiously lethargic bromine atom, and the action of methyl-alcoholic potassium hydroxide on the substance results in the production of a mixture of potassium bromide with more potassium nitrite and of a mixture of nitrophenol ethers.

EXPERIMENTAL.

5-*Bromoguaiacol* (I).

The acetyl or carbonyl derivative described below (30 grams) was dissolved in alcohol (100 c.c.), mixed with sodium hydroxide (50 grams), dissolved in a little water, and the liquid boiled under reflux during thirty minutes. The major part of the alcohol was removed by distillation, the residue acidified with hydrochloric acid, and the phenol, dissolved in ether, was finally purified by distillation in a vacuum. The fraction boiling at 150°/20 mm. constituted nearly the whole of the product, and solidified on cooling. The substance is readily soluble in most organic solvents, but may be crystallised from light petroleum, and is obtained in colourless prisms often of considerable size, melting at 65°:

0·1107 gave 0·1016 AgBr. Br = 39·1.

$C_7H_7O_2Br$ requires Br = 39·4 per cent.

This phenol is soluble in aqueous sodium carbonate solution, and gives a bluish-green coloration with ferric chloride in alcoholic solution. Its constitution follows from the conversion of the methyl ether of its dinitro-derivative into a known dinitrodiamino-anisole.

Acetyl Derivative (5-*Bromo-2-methoxyphenyl Acetate*).— 2-Methoxyphenyl acetate was readily brominated in chloroform solution by the addition of a molecular proportion of bromine dissolved in the same solvent. The solution was washed with water, dried with calcium chloride, and distilled, finally in a vacuum. A large fraction boiled at 164—165°/$\overline{2}2$ mm., and solidified completely on cooling; considerable further quantities of this fraction may be obtained by redistillation of the mixed fractions of lower and higher boiling point. The substance is readily soluble in alcohol or similar organic solvents, and crystallises from light petroleum in leaflets melting at 62—63°:

0·1439 gave 0·1053 AgBr. Br = 32·6.

$C_9H_9O_3Br$ requires Br = 32·7 per cent.

5-*Bromo-2-methoxyphenyl Carbonate*.—This derivative was obtained by the addition of bromine (25 grams) dissolved in chloroform (50 c.c.) to a solution of 2-methoxyphenyl carbonate (20 grams) (so-called guaiacol carbonate) in chloroform (50 c.c.) The bromination occurred with extreme rapidity, and the product of the reaction separated in crystals. It was collected and re-crystallised from chloroform, and obtained in colourless needles melting at 179—180°. This sparingly soluble substance is distinguished by a remarkable power of crystallisation:

0·1246 gave 0·1081 AgBr.   Br = 36·9.

$C_{15}H_{12}O_5Br_2$ requires Br = 37·0 per cent.

Since 'guaiacol carbonate' is a commercial product and the yield of the bromo-derivative is approximately theoretical, it is better to prepare 5-bromoguaiacol through the carbonate than through the acetate.

4 : 5-*Dibromoguaiacol* (II).

5-Bromoguaiacol dissolved in a little cold acetic acid was gradually treated with a molecular proportion of bromine dissolved in the same solvent. A certain amount of the product crystallised from the solution, and the remainder was precipitated on the addition of water. The solid was collected and crystallised from aqueous methyl alcohol, and obtained in slender, colourless needles melting at 95°:

0·1184 gave 0·1565 AgBr.   Br = 56·2.

$C_7H_6O_2Br_2$ requires Br = 56·7 per cent.

The substance * is freely soluble in an aqueous solution of sodium carbonate, and its alcoholic solution becomes intense ivy-green on the addition of ferric chloride. On methylation with methyl sulphate and potassium hydroxide in the usual manner, 4 : 5-dibromoveratrole was obtained. The substance was identical with the product of the direct bromination of veratrole, but the melting point of 92° was obtained after one crystallisation from alcohol, whereas the substance as usually prepared requires many crystallisations to enable it to reach an equal degree of purity, and is evidently contaminated by an isomeride.

5-*Bromo*-4 : 6-*dinitroguaiacol* (III).

After several unsatisfactory trials, the following method was found to result in a high yield of product.

Nitric acid (2·5 c.c., D 1·42) mixed with an equal volume of acetic acid was added drop by drop to a solution of 5-bromoguaiacol (2 grams) in carbon tetrachloride (15 c.c.). The mixture was vigorously shaken during the addition of the acid and the dinitro-derivative separated from the solution, and, after the addition of water, was collected and crystallised from aqueous alcohol.

* This compound is possibly identical with the dibromoguaiacol (m. p. 94—95°) which Cousin (*Ann. Chim. Phys.*, 1903, [vii], **29**, 63) obtained by the direct bromination of guaiacol in chloroform solution, although a priori it would have been anticipated that the bromination of the substance would result in 4 : 6-dibromoguaiacol.

The well-defined, rhombic prisms melt and decompose at 182—184°:

0·1372 gave 0·0874 AgBr.   Br = 27·1.

$C_7H_5O_6N_2Br$ requires Br = 27·3 per cent.

This substance is almost colourless, but dissolves in water and alcohol to bright yellow solutions. Its sodium salt is somewhat sparingly soluble, and crystallises from water in orange-yellow needles.

5-*Bromo*-4 : 6-*dinitroveratrole*, MeO⟨⟩NO$_2$ Br NO$_2$.
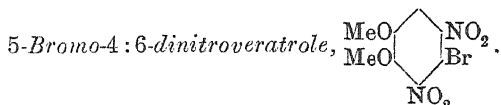
Like most dinitrophenols, the foregoing substance cannot be methylated in aqueous or alcoholic solution, and the following method was adopted with excellent results.

Bromodinitroguaiacol (15 grams) mixed with potassium carbonate (50 grams), nitrobenzene (75 c.c.), and methyl sulphate (30 grams) was heated in an oil-bath at the boiling point of the solvent during thirty minutes. The nitrobenzene was removed by distillation in a current of steam, and the residual oil easily solidified on cooling. The solid was collected and crystallised from methyl alcohol, and obtained in colourless needles melting at 102—103°:

0·1266 gave 0·0780 AgBr.   Br = 26·2.

$C_8H_7O_6N_2Br$ requires Br = 26·1 per cent.

In view of the reactivity of trinitroveratrole towards ammonia and amines, it is surprising that this substance reacts sluggishly even with boiling aqueous-alcoholic ammonia, a reagent which rapidly and quantitatively attacks the trinitro-compound, with formation of dinitrodiaminoanisole. When, however, the bromo-derivative was heated in a sealed tube at 100° during seven days with a large excess of a mixture of one volume of methyl alcohol with two volumes of concentrated aqueous ammonia, a slow conversion into the characteristic red crystals of dinitrodiamino-anisole was observed. The product was collected and washed with boiling alcohol in order to remove unchanged material, and then crystallised from nitrobenzene. The flat prisms, hæmatite-red with blue shimmer, melted at 255°, and were identified with 3 : 5-dinitro-2 : 4-diaminoanisole * (Nietzki and Kurtenacker, *Ber.*,

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* This substance is readily accessible from trinitroveratrole (Blanksma, *loc. cit.*), and serves to illustrate the effect of catalysts in the process of acetylation. It may be crystallised unchanged from acetic anhydride, and the solution in the hot solvent is intensely coloured. On the addition of a trace of sulphuric acid, the colour disappears and the colourless acetyl derivative crystallises from the solution.

1892, **25**, 282, who give m. p. 250°, and Blanksma, *Proc. K. Akad. Wetensch. Amsterdam*, 1904, **7**, 462, who gives m. p. 247°).

3 : 5-*Dinitro*-2 : 4-*dimethylaminoanisole*, $\begin{array}{c} NO_2 \\ NHMe \diagup \diagdown NHMe \\ MeO \diagdown \diagup NO_2 \end{array}$.

It was thought that the action of amines on the bromodinitro-veratrole might be more rapid than was the corresponding reaction with ammonia, but this was not markedly the case. The action of methylamine was similar to that of ammonia, and an identical process was employed. The methylamino-derivative was crystallised from alcohol, and obtained in clusters of slender, brownish-red needles melting at 158—159°:

0·1214 gave 0·1893 CO_2 and 0·0533 H_2O.   C = 42·5 ; H = 4·9.

$C_9H_{12}O_5N_4$ requires C = 42·2 ; H = 4·7 per cent.

This substance is more readily obtained from trinitroveratrole (5 grams) which was dissolved in hot ethyl alcohol (80 c.c.) and mixed with an aqueous solution of methylamine (20 c.c. of 33 per cent.). After allowing to remain during an hour, the solution was boiled under reflux for two hours, then cooled, and the separated crystals were collected and crystallised from alcohol. The substance so prepared was identified with the product obtained from bromonitroveratrole :

0·8523 distilled with 10 per cent. aqueous potassium hydroxide evolved NH_2Me, which neutralised 0·2431 HCl, whereas this amount of a substance, $C_9H_{12}O_5N_4$, yielding $2NH_2Me$, requires 0·2430 HCl.

The action of aniline in boiling alcoholic solution on bromo-dinitroveratrole resulted in the production of an orange-red substance, which it was thought should be identical with the diphenyl-amine derivative, which is obtained from aniline and trinitro-veratrole. This, however, was not the case, and the substance from the bromodinitroveratrole crystallised in red needles which darkened at 245° and did not contain bromine.

Dinitroanilinoveratrole,

$\begin{array}{c} NHPh \\ MeO \diagup \diagdown NO_2 \\ MeO \diagdown \diagup NO_2 \end{array}$ or $\begin{array}{c} NO_2 \\ MeO \diagup \diagdown NO_2 \\ MeO \diagdown \diagup NHPh \end{array}$.
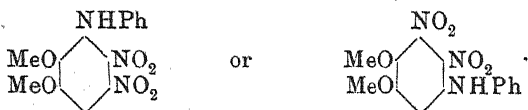
Aniline (5 c.c.) was added to a solution of trinitroveratrole (3 grams) in boiling methyl alcohol (60 c.c.), and the liquid then allowed to cool. It was then again raised to the boiling point

and the process twice repeated. The red crystals which separated did not redissolve when the solution was heated. The brilliant red needles were collected and crystallised from alcohol, and obtained in needles mixed with a small proportion of compact prisms. The prisms were picked out, and appeared to consist of an isomeride of the main product of the reaction; they have not yet been obtained in sufficient amount for satisfactory examination. The needles were recrystallised from acetic acid and then from alcohol, and melted at 199°:

0·1183 gave 0·2302 CO_2 and 0·0451 H_2O. C = 53·1; H = 4·2.
$C_{14}H_{13}O_6N_3$ requires C = 52·7; H = 4·0 per cent.

The substance is very sparingly soluble in most solvents. It is evidently to some extent of acidic character, since it yields a red solution with alcoholic potassium hydroxide and may be recovered unchanged on acidification. The solution in nitric acid soon deposits crystals of a higher nitrated derivative which is extremely sparingly soluble and crystallises from much acetic acid in orange-yellow prisms melting and decomposing at 221°. That this substance is not the expected 2 : 6-dinitro-3 : 4-dimethoxydiphenylamine is rendered highly probable by the following considerations :

(1) Ammonia and methylamine displace a nitro-group and also a methoxyl when these bases react with trinitroveratrole. Aniline, on the other hand, displaces only the nitroxyl group, and the 2 : 4-dinitrophenyl ether structure is therefore not contained in the product. The failure of aniline to attack a methoxyl group of trinitroveratrole is not due to lack of reactivity of the base, since dinitroanilinoveratrole is also resistant to the action of ammonia.

(2) Dinitroanilinoveratrole is comparatively stable towards hot aqueous potassium hydroxide.

(3) The substance is not obtained from bromodinitroveratrole by the action of aniline.

(4) The existence of two nitro-groups in the ortho-position is indicated by the following experiment : Dinitroanilinoveratrole was reduced in alcoholic hydrochloric acid solution by zinc dust, and the colourless, filtered solution added to a solution of phenanthraquinone in hot acetic acid containing sodium acetate. A condensation product was quickly formed, and crystallised from the solution in crimson needles. The substance was collected and crystallised from acetic acid, and then from ethyl acetate, and obtained in flat needles melting at 222—225°. It is doubtful whether the colour of the substance, which might be described as intermediate between mauve and crimson, is or is not due to impurity. The substance is unchanged by boiling dilute hydro-

chloric acid, and appears to be a true phenanthraphenazine. It dissolves in sulphuric acid to a red solution, quickly changing to brownish-red.

*Dinitro-*p-*toluidinoveratrole.*

This derivative, prepared by replacing the aniline in the above by *p*-toluidine, crystallised from alcohol in deep red prisms melting at 163°:

0·1302 gave 0·2571 CO_2 and 0·0542 H_2O.   C=53·9 ; H=4·6.

$C_{15}H_{15}O_6N_3$ requires C=54·0 ; H=4·5 per cent.

This substance is sparingly soluble, but less so than the aniline derivative.

LXXX.—*The Action of Halogens on Piperonal.*

By ANNIE MARY BLEAKLY ORR, ROBERT ROBINSON, and
MARGARET MARY WILLIAMS.

THE displaement of groups by nitroxyl, accompanying the nitration of phenol ethers, has frequently been observed, but it does not appear to have been recorded that a similar reaction occurs in the chlorination or bromination of certain of these substances. In the preparation of bromopiperonal in acetic acid solution, the yield of product is not satisfactory, and this caused us to suspect that a certain proportion of the formyl group is displaced by the halogen, which we found on investigation to be the case. In a neutral solvent, such as carbon disulphide or carbon tetrachloride, the yields of bromopiperonal and of 6-chloropiperonal (I) are excellent, and by-products are reduced to a minimum, but, in acetic acid solution, the bromination of piperonal produces a certain amount of 4 : 5-dibromocatechol methylene ether (this vol., p. 913), and the chlorination of the aldehyde yields 4 : 5-dichlorocatechol methylene ether (II) in addition to chloropiperonal and substances of undetermined nature which are decomposed· by aqueous sodium carbonate, and probably owe their formation to attack of the methylene ether group by the halogen. Dichlorocatechol methylene ether was also obtained by the action of chlorine on a sodium carbonate solution of piperonylic acid or of 6-chloropiperonylic acid (III) obtained by the oxidation of chloropiperonal.   4-Chloro-5-bromocatechol methylene ether (IV)

was obtained by the action of bromine on an aqueous sodium carbonate solution of chloropiperonylic acid, but not, except in traces, from chlorine and bromopiperonylic acid under similar conditions. The behaviour of chloropiperonal on nitration resembles that of bromopiperonal, and 4-chloro-5-nitrocatechol methylene ether (V) and 4-chloro-5:6-dinitrocatechol methylene ether (VI) were successively obtained. The latter on reduction furnishes a chlorodiamine, which was isolated as a phenanthra-phenazine derivative.

$$CH_2\!<^O_O\!\!\diagdown\!\!\overset{CHO}{\underset{Cl}{\diagup}}$$

(I.)

$$CH_2\!<^O_O\!\!\diagdown\!\!\overset{Cl}{\underset{Cl}{\diagup}}$$

(II.)

$$CH_2\!<^O_O\!\!\diagdown\!\!\overset{CO_2H}{\underset{Cl}{\diagup}}$$

(III.)

$$CH_2\!<^O_O\!\!\diagdown\!\!\overset{Br}{\underset{Cl}{\diagup}}$$

(IV.)

$$CH_2\!<^O_O\!\!\diagdown\!\!\overset{NO_2}{\underset{Cl}{\diagup}}$$

(V.)

$$CH_2\!<^O_O\!\!\diagdown\!\!\overset{NO_2}{\underset{Cl}{\diagup}}NO_2$$

(VI.)
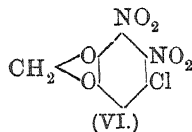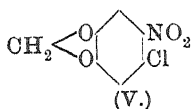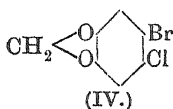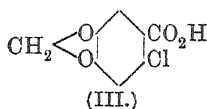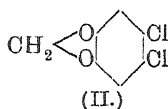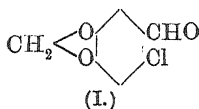
EXPERIMENTAL.

Bromination of Piperonal in Acetic Acid Solution.

Piperonal (100 grams) dissolved in acetic acid (200 c.c.) was gradually treated with bromine (40 c.c.) dissolved in acetic acid (100 c.c.), any rise of temperature being checked by cooling. After remaining overnight, the crystals were separated by filtration, and found to be pure 6-bromopiperonal (37·8 grams). The filtrate was mixed with water, and the solid collected and heated with an aqueous solution of sodium hydrogen sulphite until no further aldehyde passed into solution. The substance was then dissolved in ether and the ethereal solution extracted with repeated quantities of aqueous sodium hydrogen sulphite. The bromopiperonal was recovered from the hydrogen sulphite extract by the addition of sodium carbonate, and after crystallisation from methyl alcohol weighed 62 grams. The ethereal solution was washed with sodium carbonate and with water, dried, and evaporated, and the crystalline residue weighed 14·8 grams. It was crystallised from alcohol and identified as 4:5-dibromocatechol methylene ether, melting at 86°. The substance from this source persistently crystallised in needles, whereas it had formerly been obtained in leaflets, but the melting point of a mixture was 86°. The formation of the dibromo-derivative must be due, in the first place, to that of the monobromo-compound, in its turn obtained by a direct displacement of the formyl radicle by bromine. This

follows from the observation that bromopiperonal is stable to bromine in acetic acid solution. A specimen was found to be unchanged after the attempted reaction had been prolonged during a week.

6-*Chloropiperonal* (I).

A stream of chlorine was passed into a solution of piperonal (25 grams) in acetic acid (50 c.c.) until the product of the reaction commenced to crystallise. This required about four hours. Water was added, and the solid collected and dissolved in ether. The ethereal solution was washed with aqueous sodium carbonate and then with sodium hydrogen sulphite solution until a test portion gave no milkiness on the addition of sodium carbonate. The ethereal solution was dried and evaporated, and the residue (3·4 grams) was identified as 4:5-dichlorocatechol methylene ether. The hydrogen sulphite solutions were treated with excess of sodium carbonate, and the precipitated crystalline substance was collected and crystallised from aqueous alcohol, when 17·1 grams were obtained. The substance was further purified by crystallisation from methyl alcohol, from which it separated in long, colourless needles melting at 115°:

0·1294 gave 0·1019 AgCl. Cl = 19·3.

0·2010 in 16·06 C_6H_6 gave $\Delta^t = 0·347$. M.W. = 180.

$C_8H_5O_3Cl$ requires Cl = 19·0 per cent. M.W. = 184.

6-*Chloro*-3 : 4-*methylenedioxystyryl methyl ketone* (6-*chloropiperonylideneacetone*), $C_{11}H_9O_3Cl$, is obtained by the addition of dilute aqueous potassium hydroxide to a solution of the aldehyde in three times its weight of acetone. After an hour, water was added, and the nearly colourless precipitate collected and crystallised from alcohol. The pale yellow needles melted sharply at 158° and dissolved in sulphuric acid to a reddish-yellow solution, and the substance was recovered unchanged on the addition of water. In chloroform solution, bromine was rapidly absorbed, but the dibromide was oily.

Di-6-*chloromethylenedioxystyryl ketone*, $C_{19}H_{12}O_5Cl_2$, is obtained by the condensation of the aldehyde with the above described substance or by heating the chloropiperonal in alcoholic solution with acetone and concentrated potassium hydroxide. It is very sparingly soluble and its formation is a matter of seconds. The substance was washed with hot alcohol and crystallised from acetic acid. The felted, citron-yellow needles melted and decomposed at 265°, and dissolved in sulphuric acid to an intense blue solution which became purple and then yellow on the addition of water.

6-*Chloropiperonylic acid*, $C_8H_5O_4Cl$, was produced on oxidising

the aldehyde in benzene solution by stirring with a 2 per cent. solution of potassium permanganate. The reaction proceeds slowly, and when the benzene gave no residue on evaporation the excess of permanganate was destroyed and the acid obtained by acidification of the filtered aqueous solution. It was precipitated as a caseous solid, which was collected and crystallised from acetic acid.

The colourless needles melted at 202°, and the substance is very sparingly soluble in water. It gives a pale yellow solution in sulphuric acid, which becomes olive-green on gently heating, whereas piperonylic acid under these conditions gives an intense red solution, which may be due to a condensation in the ortho-position.

$4:5$-*Dichlorocatechol Methylene Ether* (II).

This substance may be obtained, as already mentioned, by the chlorination of piperonal, and in this case it seems that it may be obtained by the further action of chlorine on chloropiperonal, although the reaction is not smooth. It is also obtained by passing chlorine into a solution of piperonylic acid which is always kept alkaline by the addition of aqueous sodium carbonate. Finally, the same substance was prepared by chlorinating catechol methylene ether in acetic acid solution. It crystallises from alcohol in slender, colourless needles melting at 82°:

$0·1218$ gave $0·1866$ AgCl.   Cl $= 37·5$.

$C_7H_4O_2Cl_2$ requires Cl $= 37·2$ per cent.

The substance is sparingly soluble in sulphuric acid, and the solution is colourless, but becomes reddish-yellow on the addition of a trace of nitric acid. The reaction is therefore not so characteristic as that of the corresponding dibromo-derivative, which gives a rhodamine-red solution under these conditions. The constitution of the derivative follows from its production from chloropiperonylic acid, which must have the orientation of chloropiperonal, and therefore of chloronitrocatechol methylene ether, which, as shown below, must be a $4:5$-derivative.

4-*Chloro-5-bromocatechol Methylene Ether* (IV).

This substance could not be obtained by the chlorination of bromopiperonal in acetic acid solution, and only in traces, as the result of application of a large excess of reagent, by the action of chlorine on an alkaline solution of bromopiperonylic acid. It was obtained in small amount by the bromination of chloropiperonal and comparatively readily by the action of bromine on an alkaline solution of chloropiperonylic acid. It was found that

the best conditions were to add the bromine water and aqueous
sodium carbonate alternately to a dilute solution of the sodium
salt of the acid, and the completion of the reaction was judged by
the amount of the precipitate formed. This was collected and
crystallised from methyl alcohol, from which it separated in flat,
satiny needles melting at 78°.

0·1305 gave 0·1829 AgCl plus AgBr, whereas this amount of a
substance, $C_7H_4O_2ClBr$, requires 0·1838 of the mixed salts.

The reaction of this substance in sulphuric acid on the addition
of a trace of nitric acid was intermediate between that exhibited
by the dichloro- and dibromo-derivatives. The reddish-brown
solution appeared carmine in thin layers. A mixture of about
ten parts of the dichlorocatechol methylene ether with one part
of the dibromo-compound gave a solution almost identical in
appearance with that from the chlorobromo-derivative.

Application of the Cannizzaro Reaction to Piperonal.

The formation of piperonylic acid and of homopiperonyl alcohol
by the action of sodium hydroxide on piperonal does not appear
to have been described, and as we required piperonylic acid and
the alcohol was being employed in another investigation, we made
some experiments on the conditions of the reaction and adopted
the following procedure. A solution of sodium hydroxide (200
grams) in water (200 c.c.) was cooled to 40° and added to piperonal
(100 grams), contained in a bottle capable of withstanding changes
of temperature, and the mixture vigorously shaken. Alcohol
(50 c.c.) was then added, and caused an almost immediate reac-
tion and rapid rise of temperature. The bottle was vigorously
shaken and the pressure released from time to time. Soon the
temperature fell, and the mixture was then allowed to remain
overnight. It was then mixed with sufficient water to dissolve
the sodium piperonylate and extracted with benzene. The
aqueous solution gave 53 grams of piperonylic acid on acidification,
and from the benzene 1·8 grams of piperonal were recovered by
washing with sodium hydrogen sulphite solution, and after drying
the extract and removing the solvent, 32·5 grams of homopiperonyl
alcohol remained in a pure condition. It readily crystallised and
could be employed in most experiments in this condition. The
substance may be recrystallised from light petroleum, and occurs
in slender, colourless needles melting at 58°. Fittig and Remsen
(*Annalen*, 1871, **159**, 138) give the melting point as 51°, but
their product was purified by distillation.

4-*Chloro*-5-*nitrocatechol Methylene Ether* (V).

6-Chloropiperonal was dissolved in nitric acid (D 1·4), and after half an hour the mixture was added to water and the solid collected and crystallised from alcohol, in which the substance is rather readily soluble. The nearly colourless needles melted at 70° and became yellow by the action of light:

0·1231 gave 0·0867 AgCl. Cl = 17·2.

$C_7H_4O_4NCl$ requires Cl = 17·4 per cent.

This substance was also obtained from 5-nitro-4-aminocatechol methylene ether by diazotisation of the latter in hydrochloric acid and treatment with copper powder. This connects the substances described in the present communication with the series of 4 : 5-disubstituted catechol derivatives. On reduction, the substance yields a crystalline amino-derivative, which can be diazotised and contains chlorine.

4-*Chloro*-5 : 6-*dinitrocatechol Methylene Ether* (VI).

The foregoing substance was dissolved in nitric acid (D 1·52), and a rather vigorous reaction ensued which had to be moderated by cooling. On the addition of water, a precipitate was obtained which was collected and crystallised from alcohol. The sparingly soluble yellow needles melted at 138—141°:

0·1162 gave 0·0670 AgCl. Cl = 14·1.

$C_7H_3O_6N_2Cl$ requires Cl = 14·2 per cent.

This substance becomes orange-yellow on exposure to light.

4-*Chloro*-1 : 2-*methylenedioxyphenanthraphenazine*,
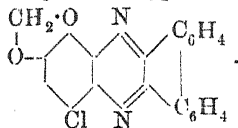
The dinitro-derivative, just described, was reduced in alcoholic aqueous hydrochloric acid solution by the addition of zinc dust, and the filtered solution, mixed with excess of sodium acetate, was heated during two or three minutes with a solution of phenanthraquinone in aqueous sodium hydrogen sulphite. The brownish-yellow precipitate was collected and dried and crystallised from xylene. Glistening, ochre-orange needles separated which melted and decomposed at 298—300°:

0·1079 gave 0·0422 AgCl.   Cl = 9·6.

$C_{21}H_{11}O_2N_2Cl$ requires Cl = 9·8 per cent.

The substance dissolves in sulphuric acid to a purple solution, and in neutral solvents to yellow solutions which exhibit intense green fluorescence.

UNIVERSITY OF SYDNEY.   [*Received September 4th*, 1917.]

LXXXI.—*Veratricsulphinide.*

By JANET FORREST McGILLIVRAY BROWN and ROBERT ROBINSON.

BAKER and Smith ("A Research on the Pines of Australia," Sydney, 1910, p. 397) have shown that the 'Huon Pine' of Tasmania (*Dacrydium Franklini*) furnishes a leaf and a timber oil which consists chiefly of eugenyl methyl ether (I), and although very considerable quantities of the substance could be rendered available from this source, there exists no outlet for the utilisation of the compound. In considering this matter, it appeared that veratricsulphinide (II), possibly a non-toxic sweetening agent, might be readily prepared from the ether, and we therefore proceeded to investigate this derivative of "saccharin," which it was found could readily be obtained by the oxidation of homoveratrole-6-sulphonamide (III) by means of an alkaline solution of potassium permanganate.
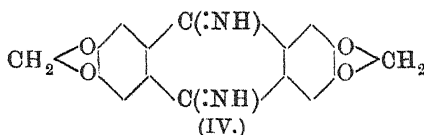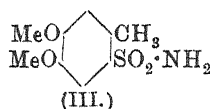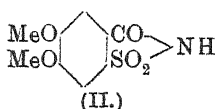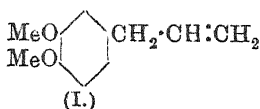
Veratricsulphinide was found to have no sweet taste. Although veratrole and homoveratrole react smoothly with chlorosulphonic acid and yield the corresponding sulphonyl chlorides in the cold and in quantitative amount, a number of veratrole derivatives behave in a somewhat abnormal manner. Eugenyl methyl ether and safrole are converted into halogen-free neutral substances which are apparently sulphonic lactones. The compound from eugenyl methyl ether crystallises from alcohol in leaflets melting

at 145°, and the investigation is being continued. Chlorosulphonic acid converted the nitrile of piperonylic acid into a dimeride, to which we ascribe the constitution IV.

<div align="center">EXPERIMENTAL.</div>

<div align="center">*Veratrole-4-sulphonyl Chloride.*</div>

This substance has been prepared by Paul (*Ber.*, 1906, **39**, 2773) from veratrole-4-sulphonates. The following direct process is convenient and the yield is quantitative. A solution of chlorosulphonic acid (40 grams) in chloroform (120 grams) was gradually added to veratrole (20 grams), when a vigorous reaction occurred. After allowing to remain during an hour, water was added and the chloroform solution dried and evaporated. The solid residue was sufficiently pure for most experiments, but a portion was crystallised from a mixture of benzene and light petroleum, and the colourless needles melted at 71°.

The sulphonamide was also prepared, and melted at 136° after crystallisation from alcohol.

<div align="center">5-*Nitroveratrole-4-sulphonyl Chloride,*</div>

<div align="center">MeO⟨⟩NO$_2$
MeO⟨⟩SO$_2$Cl ·</div>
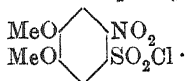
Nitric acid (75 c.c., D 1·42) was added with cooling to veratrolesulphonyl chloride (30 grams), and after an hour the mixture was poured into water and the nitro-derivative collected and crystallised from acetic acid. The pale yellow needles melted at 128°:

0·1223 gave 0·0613 AgCl. Cl = 12·3.

$C_8H_8O_6NClS$ requires Cl = 12·5 per cent.

When this substance (10 grams) was boiled with potassium hydroxide (10 grams) in water (100 c.c.) during a minute and a half, it dissolved to an orange ·liquid, which became yellow on neutralisation with hydrochloric acid. On cooling, potassium nitroveratrolesulphonate separated almost completely as a bright yellow, crystalline powder. This was washed with a little water and dried at 100°:

0·1355 gave 0·1006 BaSO$_4$. S = 10·4.

0·1635 ,, 0·0468 K$_2$SO$_4$. K = 12·8.

$C_8H_8O_7NSK$ requires S = 10·6; K = 13·0 per cent.

On boiling with nitric acid, this salt was converted into 4 : 5-dinitroveratrole, which is a proof that the constitution assigned to the nitroveratrolesulphonyl chloride is correct.

5-*Nitroveratrole*-4-*sulphonamide* crystallised from alcohol in pale yellow needles melting at 132°.

<p style="text-align:center">5-*Aminoveratrole*-4-*sulphonic Acid*,</p>

$$\text{MeO} \overset{\displaystyle\bigwedge}{\underset{\displaystyle\text{MeO}}{}} \text{NH}_2$$

MeO⟨⟩NH₂
MeO⟨⟩SO₃H .

Considerable quantities of this acid were required for some synthetical experiments, and the following procedure was adopted after a number of trials. The yield was 78 per cent. of that demanded by theory, and, indeed, the whole preparation of the substance from veratrole is a simple operation involving but small loss of material. It was found best to carry out the reduction on the scale described. Hydrochloric acid (25 c.c.) was added to a mixture of potassium nitroveratrolesulphonate (5 grams) and crystallised stannous chloride (15 grams). Heat was developed, the nitrosulphonate passed into solution, and the aminosulphonic acid crystallised. Hot water (50 c.c.) was added and the mixture allowed to cool, after which the solid was collected and recrystallised by solution in hot aqueous sodium carbonate and reprecipitation by hydrochloric acid. The substance is sparingly soluble, even in hot water, and crystallises in small, hard, colourless prisms, which were dried at 120° without suffering change in appearance :

0·1338 gave 0·1319 $BaSO_4$.   S = 13·5.

$C_8H_{11}O_5NS$ requires S = 13·7 per cent.

0·1709 neutralised 0·0290 NaOH, whereas this amount of a monobasic acid, $C_8H_{11}O_5NS$, requires 0·0293 NaOH.

Like other derivatives of veratrylamine, this substance develops an intense blue coloration with ferric chloride in aqueous solution. On addition of hydrochloric acid to a fairly concentrated solution of the amino-sulphonic acid in potassium carbonate to which rather more than a molecular proportion of sodium nitrite had been added, the diazonium derivative is readily produced and separates in colourless crystals. This compound is doubtless of the type of diazobenzenesulphonic acid, and is relatively stable. It couples with β-naphthol to a crimson azo-compound, and retains this power even after boiling its aqueous solution for a short time. On adding potassium iodide to an aqueous suspension of the diazo-derivative, nitrogen was evolved, and the potassium salt of an iodosulphonic acid crystallised from the solution. When pure nitroveratrolesulphonyl chloride was employed in the preparation of the amino-acid, the substance described was the sole product isolated, but, on the other hand, when the crude product was utilised without purification, then the acid mother liquor, from

which the 5-aminoveratrole-4-sulphonic acid had been separated, slowly deposited long needles on keeping in the ice-chest.   The substance is very probably 3-*aminoveratrole-4-sulphonic acid*, and its formation is a proof of the presence of a small proportion of an isomeride in the product of the nitration of veratrolesulphonyl chloride.   After recrystallisation from water, colourless needles containing solvent of crystallisation were obtained, and the analytical results were rather unsatisfactory until the material was dried at 120° :

0·1310 gave 0·1299 $BaSO_4$.   S = 13·6.

$C_8H_{11}O_5NS$ requires S = 13·7 per cent.

This substance was produced in such small amount that a complete examination was impossible, but it was found to be distinguished from its isomeride by its greater solubility in water and by crystallising in needles instead of prisms.   With ferric chloride it gives an orange coloration in aqueous solution.   The substance appears to be oxidised by nitrous acid, but with the aid of β-naphthol sufficient evidence of the presence of a primary amino-group was obtained.

Homoveratrole-6-sulphonamide (III).

Homoveratrole (60 grams) was converted into the corresponding sulphonyl chloride by the action of chlorosulphonic acid exactly as described above for the preparation of vertatrolesulphonyl chloride, but in this case the product was an oil which could not be crystallised.   The substance was therefore converted into the sulphonamide by mixing with aqueous ammonia (250 c.c., D 0·88), when a vigorous reaction ensued and a colourless, crystalline substance was produced.   This was collected, washed with water, and recrystallised from alcohol, and the yield obtained was 80 per cent. of that theoretically possible.   The substance crystallised from alcohol in prismatic needles and from ethyl acetate in compact prisms melting at 191° :

0·1147 gave 0·1959 CO_2 and 0·0584 H_2O.   C = 46·6; H = 5·7.

0·1215   „   0·1228 $BaSO_4$.   S = 13·9.

$C_9H_{13}O_4NS$ requires C = 46·7; H = 5·6; S = 13·9 per cent.

This substance is far more sparingly soluble than veratrolesulphonamide, and advantage might possibly be taken of this in order to estimate the percentage of guaiacol in specimens of creosol.

Veratric-6-sulphinide, " *Dimethoxysaccharin* " (II).

Homoveratrolesulphonamide (25 grams) dissolved in a solution of potassium hydroxide (10 grams) in water (500 c.c.) was oxidised at 80° by the gradual addition of potassium permanganate (70 grams) dissolved in hot water (850 c.c.). When all the permanganate was reduced, the filtered solution was cooled and saturated with carbon dioxide, when a small quantity of unchanged sulphonamide was recovered. The liquid was evaporated until crystals began to separate from the hot solution, which was then allowed to cool. The solid was collected, and found to consist of a potassium salt, which was accordingly dissolved in water and the solution acidified with hydrochloric acid. The colourless precipitate was collected and crystallised from much acetic acid. The substance was extremely sparingly soluble in most organic solvents and also in water. It dissolved, however, in boiling water to some extent, and separated on cooling in fern-like aggregates of needles:

0·1096 gave 0·1773 CO_2 and 0·0375 H_2O.   C = 44·1; H = 3·8.

0·1338 ,, 0·1270 $BaSO_4$.   S = 13·0.

$C_9H_9O_5NS$ requires C = 44·4; H = 3·7; S = 13·2 per cent.

The melting point of this compound is not sharp, as it commences to soften at 275° and is completely fused at 290°.

It is entirely devoid of sweet taste, and is, on the contrary, slightly acid and bitter. Its acidic properties are well marked, as it readily dissolved in cold aqueous sodium carbonate and even in warm sodium acetate solution. The sodium salt crystallises from water in glistening needles and has no sweet taste. The substance is very stable towards alkali, and even on fusion with potassium hydroxide there is little sign of decomposition. However, the methoxy-groups are so hydrolysed, since, on dissolving the fusion in water, acidifying, and extracting with ether, the extract can be shown to contain a catechol derivative by the usual test, although the intense bluish-green with ferric chloride and the Bordeaux-red obtained on the addition of sodium carbonate are far more characteristic than is the case with catechol itself.

N-Methyl Derivative.—This substance is readily obtained by warming and shaking a solution of the sulphinide in aqueous sodium carbonate with methyl sulphate. It separates from the alkaline solution in colourless crystals and may be recrystallised from alcohol, in which it is sparingly soluble. In appearance it resembles the mother substance and crystallises in fronds, which are aggregates of needles melting at 227°:

0·1209 gave 0·1106 $BaSO_4$. $S = 12·6$.

$C_{10}H_{11}O_5NS$ requires $S = 12·5$ per cent.

The substance is insoluble in cold dilute aqueous potassium hydroxide, but on boiling gradually passes into solution as the result of hydrolysis.   On acidification there is no precipitate in the cold, but on boiling the solution, separation of N-methyl-veratricsulphinide occurs.   The substance was collected, and melted at 227°.

2 : 3 : 6 : 7-*Dimethylenetetraoxyanthraquinonedi-imide* (IV).

The direct sulphochlorination of derivatives of veratric and piperonylic acids was investigated in the hope of discovering a convenient approach to the substituted "saccharins," but the results were usually negative.   The action of chlorosulphonic acid on the nitrile of piperonylic acid resulted, however, in the formation of an anthraquinone derivative of a new type.

The nitrile (5 grams) was dissolved in chloroform (15 c.c.) and chlorosulphonic acid (7 grams) gradually added.   The liquid became dark red, heat was developed, and, after the initial reaction had subsided, the mixture was heated on the steam-bath during one minute.   It was then cooled and mixed with acetic acid, when an orange-red substance separated, which was collected and washed with ether.   This substance appeared to be a salt, and was warmed with a solution of sodium acetate and so changed to a nearly colourless, flocculent precipitate, which was collected, washed with water, and dried, and then crystallised from nitrobenzene and again several times from xylene.   The clumps of colourless, microscopic needles melted at 261°:

0·1208 gave 0·2891 CO_2 and 0·0377 H_2O. $C = 65·3$; $H = 3·5$.

0·1300   ,,   10·7 c.c. N_2 at 20° and 765 mm. $N = 9·6$.

$C_{16}H_{10}O_4N_2$ requires $C = 65·3$; $H = 3·4$; $N = 9·5$ per cent.

The compound is very sparingly soluble and dissolves in sulphuric acid to a rich crimson solution, which becomes yellow on the addition of water.   The solution resembles in colour-tone those which are obtained from methoxyanthraquinones and sulphuric acid, and on this account, and in view of the results of analysis, the constitution suggested appears probable.   Nevertheless, only a mere trace of anthracene was obtained by boiling with hydriodic acid followed by distillation of the washed product over zinc dust in a stream of hydrogen.   The amount obtained from 2 grams enabled us to recognise anthraquinone, obtained on oxidation, by the oxanthranol reaction.   The substance appears to be remarkably resistant to hydrolysis and is unchanged by boiling hydro-

chloric acid. Should opportunity offer, the properties of this substance and some analogous compounds, which have been prepared, will be further investigated.

UNIVERSITY OF SYDNEY.

LXXXII.—*Researches on Pseudo-bases. Part II.** *Note on some Berberine Derivatives and Remarks on the Mechanism of the Condensation Reactions of Pseudo-bases.*

By GERTRUDE MAUD ROBINSON and ROBERT ROBINSON.

THE analogy between berberine and cotarnine was spectrochemically demonstrated by Tinkler (T., 1911, **99**, 1340), and in view of the fact that the former base contains an unreduced *iso*quinoline nucleus, it became of interest to examine its behaviour in connexion with the formation of condensation products analogous to the numerous anhydrocotarnine derivatives. Anhydroberberineacetone (I) (ψ-B-CH_2·COMe) is the only substance of this type which has been investigated. It was prepared by Gaze (*Zeit. Naturwiss. Halle*, 1890, **62**, 399), and its analogy to anhydrocotarnineacetone was pointed out by Gadamer (*Arch. Pharm.*, 1905, **243**, 42) and confirmed by the examination of the substance which was made by Pyman (T., 1911, **99**, 1694).
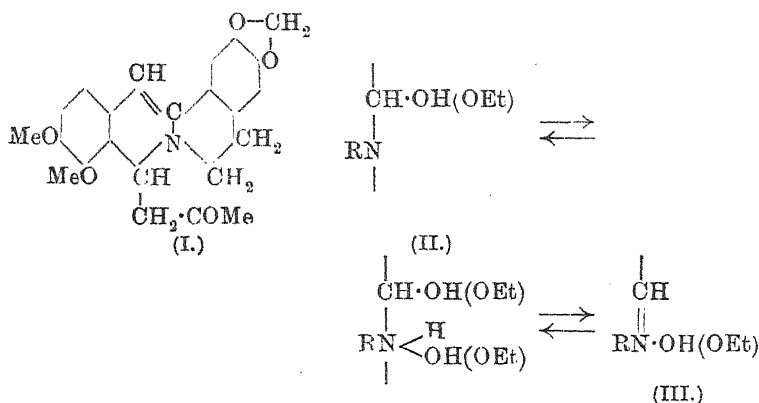
* Part I (T., 1914, **105**, 1456) contains the following errata on page 1458 : for *6-nitropiperonylhydrocotarnine* read *6-nitropiperonoylhydrocotarnine* and for *anhydrocotarnine-6-nitroveratrole* and *6-nitroveratrole* read *anhydrocotarnine-6-nitrohomoveratrole* and *6-nitrohomoveratrole* respectively.

It was found in small-scale experiments that berberine condensed readily with alcohols, amides, such as carbamide, phthalimide, 2-methylindole, acetophenone, 1-hydrindone, *cyclo*hexanone, nitromethane, 2 : 4-dinitrotoluene, 2 : 4 : 6-trinitrotoluene, diethyl malonate, ethyl acetoacetate, ethyl phenylacetate, phenylacetonitrile, and indene. Berberinol (compare Tinkler, *loc. cit.*) was dissolved in alcohol, and, after the addition of one of the compounds mentioned, the mixture was gently warmed. As a rule, a sparingly soluble substance separated, often in a viscid condition, but crystallisable after treatment, usually by washing with alcohol, and the derivatives were lemon-yellow with the exception of the nitro-compounds, which were orange or red. All the substances were resolved into their components by acids, and anhydroberberine derivatives are therefore much less stable than the corresponding substances obtained from cotarnine or hydrastinine. Circumstances forced the authors to abandon the detailed examination of these substances at a time when the work had not proceeded far and was quite incomplete, but it nevertheless now seems desirable to record the results of the investigation. Cyano-dihydroberberine (ψ-B-CN), methoxydihydroberberine (ψ-B-OMe), anhydroberberineacetophenone (ψ-B-CH$_2$·COPh), and anhydroberberinenitromethane (ψ-B-CH$_2$·NO$_2$) are described in the experimental portion of the paper.

The Mechanism of Pseudo-base Condensation.

The fact that berberine resembles cotarnine in its reactions emphasises the probability that the reactive modification is in each case the quaternary ammonium hydroxide form, since berberine has an even greater tendency than cotarnine to assume this unsaturated condition. The formation of anhydroberberineacetone was found to occur in dilute alcoholic solution under conditions not favourable to the existence of berberinol, and a hitherto unrecorded observation on the condensation of cotarnine with nitromethane may also be cited. A dilute aqueous acetic acid solution of cotarnine was mixed with nitromethane, and on the addition of sodium acetate the condensation product was formed, slowly in the cold, rapidly on heating the mixture, and the substance was identified with anhydrocotarninenitromethane (Hope and Robinson, T., 1911, **99**, 2119). In this acid solution the presence of the carbinol form of cotarnine is extremely improbable. At the same time, condensation products are obtained from cotarnine and berberine under conditions which do not favour electrolytic dissociation of an ammonium hydroxide. Thus the presence of an excess of sodium hydroxide does not appear to

inhibit the reactions. A representation of the mechanism of the Knoevenagel reaction, based on the assumption of a reaction between ions, was suggested by Lapworth (Hope and Robinson, *loc. cit.*, 2117), and was a great advance on the ideas existing at that time, especially as it facilitated the collation of data derived from such separate investigations as those of Knoevenagel on the use of amines, particularly secondary amines, as catalysts in condensations, of Dobbie, Lauder, and Tinkler on the spectrochemistry of pseudo-bases, and of numerous workers on the chemistry of these substances. These advantages are secured by the recognition that the reactive form of a carbinol-amine (II) is the unsaturated ammonium hydroxide (III), but instead of representing the further stages as due to ionisation, combination of the ion with a negative residue, and, finally, migration, the present authors prefer to regard the condensations as due to a simple addition of the components as illustrated in the scheme :
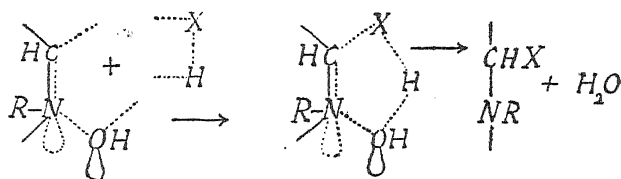
In the case of a condensation between a pseudo-base and pseudo-acid, the theory of the reaction between ions demands two intramolecular changes, but on the hypothesis now advanced the carbon to carbon synthesis occurs in the first stage of the process and migrations are not required. This is illustrated in the case of anhydrocotarninenitromethane, and it will be seen that the *aci*-modification of nitromethane and the ammonium hydroxide form of cotarnine yield a complex (IV) in which there may be a change in affinity distribution which results in the separation of water and the production of anhydrocotarninenitromethane.

(IV.)
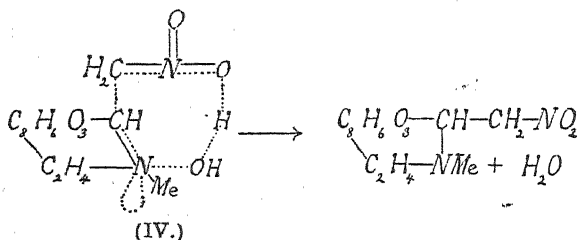
The essential feature of these representations is the postulation of conjugated partial dissociation as a preliminary stage of the

reactions, and this is a particular case of the process described by Baly as "opening up the molecular force fields." The mode of expression is, however, slightly different from that employed in a former communication (T., 1916, **109**, 1031 * *et seq.*, 1042).

Taking methyl iodide as an example, then, in reactions in which the iodine becomes separated from the methyl group, it is assumed that there is a partial dissociation and that the reactive molecule should be represented as ...CH_3I.... The present suggestion is merely that the partial valency so expressed shall be considered to be derived from the normal valencies and that the dissociation necessarily weakens the bond between the carbon and iodine atoms, so that the complete symbol is ...CH_3...I.... Where a partial dissociation can be followed by complete electrolytic dissociation, there is a clue to the polarity of the partial valencies, since it may reasonably be assumed that the partial dissociation is a stage in the complete process. Further, it is clear that the partial dissociation of latent valencies must be assumed in some cases, as, for example, in the combination of ammonia with hydrochloric acid :

$$C\!\cdot\!NH_3 \rightleftarrows C\!\cdot\!N\!H_3 \;+\; \begin{matrix} \cdots H \\ | \\ \cdots Cl \end{matrix} \;\rightleftarrows\; C\!\cdot\!N\!H_3\; \begin{matrix} H \\ | \\ Cl \end{matrix} \;\rightleftarrows\; NH_4Cl$$
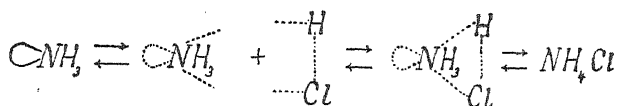
The conjugated partial dissociation of such an ammonium hydroxide as cotarninium hydroxide is a more complex example of the same kind :

$$H\,\overset{|}{\underset{|}{C}} \qquad H\,\overset{|}{\underset{}{C}} \qquad H\,\overset{|}{\underset{}{C}}$$
$$Me\!\cdot\!N\!-\!OH \;\longrightarrow\; Me\!\cdot\!N\cdots OH \;\longrightarrow\; Me\!\cdot\!N\cdots OH$$
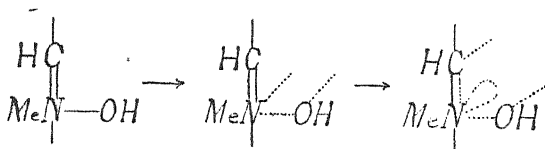
* In this paper, the residual affinity was regarded as additional to the normal valency, not as a part of the latter. The theory of the reactions is not fundamentally altered, and in accordance with the suggested method of expression the addition of an alkyl haloid to an unsaturated base would be represented by the scheme:

$$c\!\cdot\!C\!\!\begin{matrix}N\!:\!ab\\ \\de\!:\!C\end{matrix} \;+\; \begin{matrix}\cdots x\\ \\ \cdots y\end{matrix} \;\longrightarrow\; c\!\cdot\!C\!\!\begin{matrix}N\!:\!ab\\ x\\ \\de\!:\!C\quad y\end{matrix} \;\longrightarrow\; c\!\cdot\!C\!\!\begin{matrix}N\!:\!abx\\ \\C\!:\!dey\end{matrix}$$
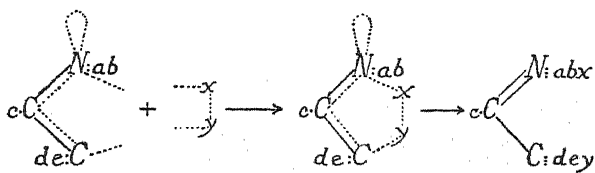
In partial dissociation of latent valencies, two partial valencies of opposite sign become available, and these emanate from the same atom, whereas when a normal valency is divided, the two parts will be of the same sign, so that the ring in IV in regard to the polarity of the partial valencies should be expressed as shown below :

$$C = + N = + = O$$
$$C^+_+ \qquad {}^+_+ H$$
$$C = N = + = O$$
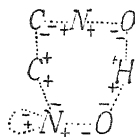
The logical application of schemes of partial dissociation, simple and conjugated, of addition and decomposition by making and breaking of partial valencies, and of redistribution of affinity, demands the consideration of these questions of polarity and leads to a system of mechanism of reactions which appears to be capable of including the representation of chemical changes of the most varied type, and the present authors are not acquainted with any examples of reactions the course of which cannot be illustrated in the manner implied. It is true that the subdivision of units invariably supplies greater facilities for explanations, but in the present instance there is the important restriction on the elasticity of the theory which is imposed by the necessity of providing the reactive complexes with two free partial valencies of opposite sign, and this has introduced no difficulty in any case examined. In order to avoid possible misapprehension, it should be stated that reactions between ions are not excluded, but regarded as the limiting case, and, further, that it is recognised that the symbols which are used to express the activated condition of molecules can represent only a first approximation to the actual distribution of affinity.

We cannot deal with every instance in which it is imagined that the method of representation advocated has clear advantages in the summarisation of the experimental data, and we therefore confine ourselves to two reactions which have been the subject of comparatively recent controversy.

The Bromination of Ketones.

Lapworth's theory of the mechanism of the bromination of acetone and other ketones (T., 1904, **85**, 30) has received much support from subsequent experimental work, and it may be said to be universally accepted that the essential reaction is the addition of bromine to the enolic form of the ketone. Leuchs (*Ber.,*

1913, **46**, 2435), however, brominated optically active *o*-carboxy-2-benzyl-1-hydrindone and obtained 5—10 per cent. of an optically active bromo-derivative, and since the enolic form of this ketone contains no asymmetric carbon atom, it was claimed that the bromination was in part a direct substitution. In accordance with the theory of partial conjugated dissociation of an enol, however, the actual reactive conditions is not
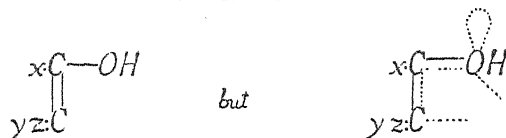
and this reactive form is seen to be intermediate as regards its distribution of affinity between the ketone and its enolic modification. Consequently, the catalytic action of hydrobromic acid on the ketone in producing the enol will involve the reactive form of the latter as an intermediate stage. In this molecule, the partial valency preserves the asymmetric environment of the carbon atom, and the formation of an optically active bromo-derivative is therefore possible. The whole process may be represented in the following manner:
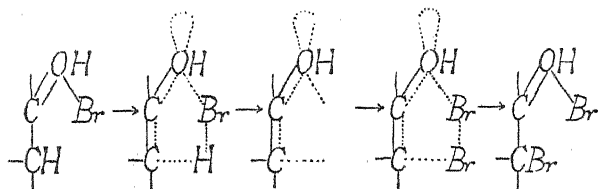
Mechanism of Diazo-coupling.

K. H. Meyer (compare "Annual Reports," 1914, **11**, 100; 1915, **12**, 115) and his co-workers hold the view that diazo-coupling is due to an addition of the diazonium salt to a double bond or conjugated double bond in the second component. Other authors, as Auwers and Michaelis, and Karrer (*loc. cit.*), are of the opinion that the reaction is in the first place one of addition to the oxygen or nitrogen atom of the phenol or amine, and that this is followed by migration. Both these views are experimentally founded and at present regarded as contradictory. The application of the theory of addition of partly dissociated complexes leads to a representation which in the present authors' opinion explains the whole of the facts, including those relating to the chemistry of the diazonium salts themselves. It has already been suggested (T.,

1916, **109**, 1042) that the characteristic reactions of aromatic
amines and phenols must be ascribed to additions to a conjugated
unsaturated system which includes the nitrogen or oxygen atoms.
The neutral and reactive phases of a phenol, such as *m*-cresol, will
therefore be the following:
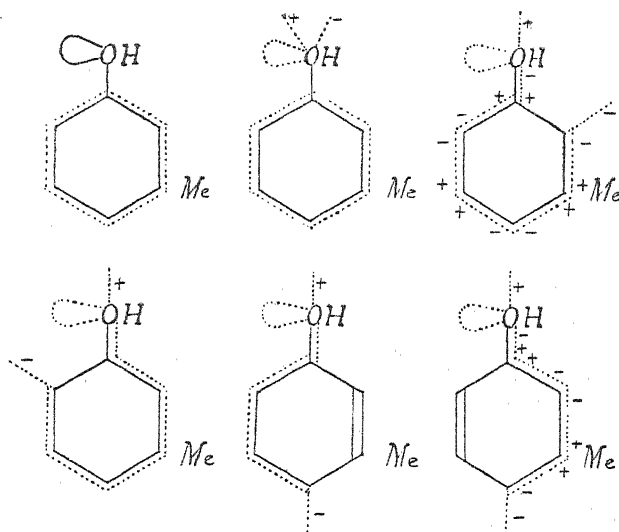
An examination of the polar properties of the partial valencies
shows that the orientation rules are a direct consequence of the
opposite sign of the latent valencies of elements, such as oxygen
and nitrogen, but it must be remembered that in dealing with
amines and phenols the effects observed are considerable and well
defined, and that in connexion with the general problem of
orientation in the benzene ring it may be necessary to take
cognisance of even more delicate influences than the conjugation
of partial valencies. The reactive phases of an aromatic amine
will correspond with those figured above in the case of *m*-cresol.
Addition to the unconjugated reactive modifications will involve
the attachment of a group to the oxygen or nitrogen atoms,
whereas addition to the molecule in its conjugated dissociated
condition will involve nuclear substitution. If the former reac-
tion is reversible, and this is usually the case, there may ensue an
apparent transference of a group from oxygen or nitrogen to the
nucleus, and the transformation of diazoamino-compounds into
true azo-derivatives is not improbably a reaction of this type.
The phenomenon is analogous to that involved in the production

of mesidine from phenyltrimethylammonium chloride, and as this is a simpler case, the first stage of the process may be illustrated:
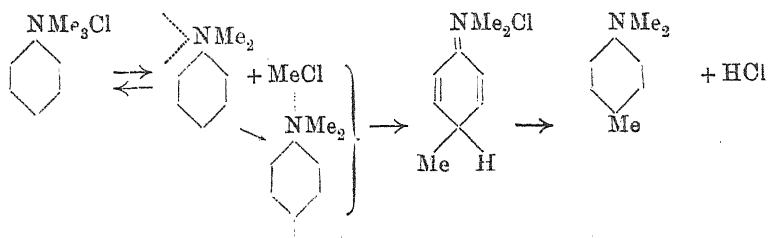
The last reaction is a conjugated decomposition, that is, the reverse of addition to a conjugated system. Such reactions are of great importance in the aromatic series, and there appears to be no valid reason why the decomposition should have a more complex mechanism than the formation of the additive product.

Turning to the diazonium compounds, it must be noted that these substances (for example, hydroxides) are in constitution and properties strikingly analogous to such substances as cotarninium hydroxide and owe their reactivity to a similar partial decomposition, which is expressed in V. Addition between the reactive phases of a phenol and of a diazonium hydroxide will result in VI, and possibly VII may then be obtained by a redistribution of affinity.

(V.)　　　　(VI.)　　　　(VII.)
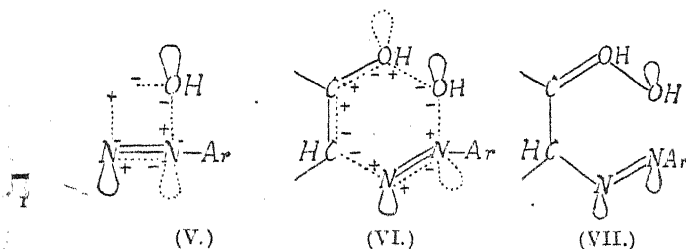
VII is clearly the oxonium hydrate of the keto-form of an azo-phenol, but it is also the hydrate by conjugated addition of the enolic modification, and the latter may be obtained by conjugated decomposition as shown above for the precisely similar conversion of a ketone into an enol with the aid of hydrobromic acid. It should be pointed out, however, that it is unnecessary to go so far as VII in rearranging the affinity of VI. If, for example, the partial valency connecting the nitrogen atoms is broken, the natural result of the activity of the free partial valencies is indicated in VIII, IX, and X.

The above will apply to a phenol, such as β-naphthol, which couples in the ortho-position. Para-substitution will involve the inclusion of an additional double bond in the conjugated system, and it is clear that the scheme is applicable to amines as well as to phenols.

(VIII.)   (IX.)   (X.)
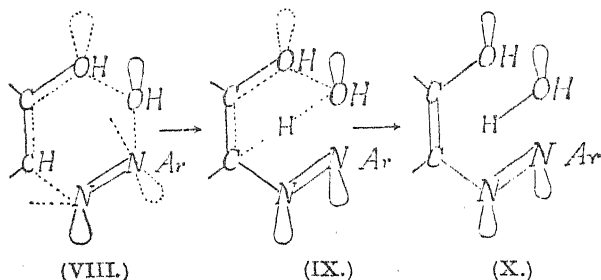
EXPERIMENTAL.

Cyanodihydroberberine.

This substance was prepared by Henry (*Annalen*, 1860, **115**, 136), and regarded as a sparingly soluble salt which crystallised from alcohol in yellow, rhombic leaflets. The analysis given is 3 per cent. lower than the theory, and indeed at that time the composition of berberine was supposed to be $C_{42}H_{19}O_{10}N$ ($C=6$; $O=8$). In 1872 Flückiger (*Jahresber.*, 748) stated that the substance did not exist, and later Pommerehne (*Arch. Pharm.*, 1895, **233**, 127) reaffirmed that berberine forms a stable hydrocyanide. Tinkler (*loc. cit.*) used the substance in connexion with his spectrochemical work. Since it appears that this compound has not yet been accurately analysed or described, we prepared a specimen by adding potassium cyanide to a solution of berberine sulphate until the yellow colour disappeared. The solid was collected and rapidly crystallised from alcohol and then from benzene, in which the substance is sparingly soluble. It was found necessary to keep the solution in the dark, as the compound is decomposed by light. The pale yellow prisms melted at 184—186° when somewhat rapidly heated:

0·1405 gave 0·3602 CO_2 and 0·0661 H_2O. $C=69·9$; $H=5·0$.

$C_{21}H_{18}O_4N_2$ requires $C=69·6$; $H=5·2$ per cent.

The substance is readily soluble in chloroform and sparingly so in ethyl acetate, from which it crystallises in yellow octahedra. It is stable towards aqueous potassium hydroxide and is not immediately decomposed by cold dilute hydrochloric acid. On gently warming, hydrocyanic acid and berberine chloride were

produced. No definite evidence of the formation of a salt of the base was obtained, but that substances of this type are real bases which can form salts without decomposition is evident from the behaviour of cyanohydrocotarnine. This substance dissolves in dilute sulphuric acid, but, on scratching the container, colourless crystals of a sparingly soluble sulphate separate. Only on heating does the colourless solution become yellow, and hydrocyanic acid is then set free. It is a mistake, therefore, to term these substances pseudo-salts. They are in no sense salts, but bases which can combine with acids, and in this condition are readily decomposable. We have also observed that cyanohydrocotarnine forms a methiodide.

Methoxydihydroberberine, ψ-B-OMe.

Perhaps the most characteristic reaction of pseudo-bases is the formation of ethers of the carbinol form by simple treatment with alcohols, and it is interesting to note that this property is exhibited, not only by the rosaniline bases, but also by many triphenylcarbinol derivatives not containing nitrogen and by the xanthhydrols and other pseudo-oxonium bases. In the presence of excess of water, these ethers are as readily hydrolysed as they were formed, and the conclusion to be drawn from the whole matter seems to be that the interconversion of the two forms of the pseudo-base is accomplished by addition and subtraction of water or of an alcohol. Gaze, in a private communication to Beilstein's " Handbuch," states that berberine yields an alcoholate, $C_{20}H_{17}O_4N,C_2H_6O$, which he describes as golden crystals, but there appear to be no further references in the literature to substances of this type. Berberinol (15 grams) was added with stirring to methyl alcohol (35 grams), when the substance became more crystalline in appearance. After remaining during two hours, the substance was collected and rapidly crystallised from methyl alcohol. It was obtained in pale yellow prisms melting at 152°:

0·1239 gave 0·3126 CO_2 and 0·0661 H_2O.　C = 68·8 ; H = 5·9.

$C_{21}H_{21}O_5N$ requires C = 68·7 ; H = 5·7 per cent.

In attempting to crystallise this substance from ethyl acetate, oxyberberine melting at 198—200° was obtained. The substance was also readily changed to oxyberberine by boiling with sodium methoxide in methyl-alcoholic solution. It appears to be more easily oxidised than berberinol itself Like most dihydroberberine derivatives, the dilute solution in ethyl acetate exhibits blue fluorescence. The methoxy-group was readily removed in the form of methyl alcohol on warming the substance with water.

Ethoxydihydroberberine.—This derivative crystallised in golden-yellow, rectangular prisms which darken at 125° and melt at 136°. Its properties were similar to those of the methoxy-compound. In absolute ethyl alcohol the substance condensed readily with acetone, producing anhydroberberineacetone melting at 175°.

iso*Amyloxydihydroberberine.*—This substance was obtained in circular clusters of golden needles and melted at 157°. Its ethyl acetate solution exhibits blue fluorescence.

Anhydroberberineacetophenone, ψ-B·CH$_2$·COPh.

This derivative was obtained by condensing berberinol with acetophenone in alcoholic solution or by starting with methoxydihydroberberine and carrying out the reaction in absolute methyl-alcoholic solution. It is, however, more convenient to operate in the following manner. Berberine sulphate (20 grams) was mixed with alcohol (100 c.c.) and acetophenone (10 grams), and, after gently heating the mixture, a 20 per cent. aqueous solution of potassium hydroxide was added until the orange colour became red and then yellow. The liquid was vigorously stirred, and, after the addition of water, the yellow oil gradually solidified and was collected and crystallised, first from alcohol, in which the substance is sparingly soluble, and then from ethyl acetate. The final purification was by crystallisation from benzene containing a little light petroleum, and the substance was then obtained in 0·131 yellow prisms melting at 140—141°:

0·1 gave 0·3542 CO$_2$ and 0·0658 H$_2$O.   C = 73·7 ; H = 5·6.

This compound C$_{25}$O$_5$N requires C = 73·8 ; H = 5·5 per cent.

berberine salt and acetophenone, decomposed by acids, yielding a even when the compound is warmed with water of which is perceptible was changed by methyl sulphate into what appeared to be a mixture of metho-salts with berberinium sulphate. On boiling the golden-yellow mixture with hydrochloric acid, acetophenone was liberated, and a salt separated which had the appearance of berberinium chloride, but was contaminated with a considerable proportion of some analogous compound. The mixture could not be separated into its constituents, but analysis indicated that it consisted of berberinium chloride and a methylberberinium chloride.

Anhydroberberinenitromethane, ψ-B·CH$_2$·NO$_2$.

Berberine sulphate (20 grams) was warmed with a mixture of ethyl alcohol (100 c.c.) and water (100 c.c.) and treated with

concentrated solution of potassium hydroxide until a clear solution was obtained. Nitromethane (10 c.c.) was then added and more dilute potassium hydroxide gradually introduced, care being taken not to render the solution strongly alkaline. A crystalline, red precipitate was formed, which was collected and recrystallised from alcohol. The orange-red needles melted at 140°. Recrystallisation from alcohol resulted in lowering of the melting point to 136°, but from toluene, orange, prismatic needles melting at 142° were obtained:

0·1165 gave 0·2733 CO_2 and 0·0582 H_2O.   C = 63·9; H = 5·5.

$C_{21}H_{20}O_6N_2$ requires C = 63·6; H = 5·1 per cent.

This substance is changed by acids into a berberine salt. It was also obtained by condensation of methoxydihydroberberine and nitromethane in methyl-alcoholic solution.

UNIVERSITIES OF SYDNEY AND LIVERPOOL.

LXXXIII.—*The Absorption Spectra of some Polyhydroxyanthraquinone Dyes in Concentrated Sulphuric Acid Solution and in the State of Vapour.*

By DAVID B. MEEK.

IN a previous communication (Meek and Watson, T., 1916, **109**, 544 *et seq.*) on the colour of the polyhydroxyanthraquinone dyes it was shown that the wave-length of the maximum of an absorption band of any of the substances depended on whether the substance was examined in alcoholic solution, in potassium hydroxide solution, or on cloth variously mordanted. Taking the absorption as due to the resonance produced in a system capable of oscillating between the different tautomeric forms, then this period of oscillation was regarded as modified by the nature of the radicle attached to the conjugate chain of double and single bonds. One of the conclusions drawn from that investigation was that "the more electropositive the nature of the radicle attached to a conjugate chain, the longer will be the wave-length of the maximum of the absorption band." In that work the spectrum of each of the dyes was examined, (1) in alcoholic solution, (2) in aqueous potassium hydroxide solution, and on wool mordanted with (3) tin, (4) alum, and (5) chrome respectively. The present investigation was undertaken with a view to obtain information regarding the

absorption spectra of the same polyhydroxyanthraquinone dyes in solution in concentrated sulphuric acid and in the state of vapour. Some of these dyes had given a number of fairly narrow, sharp bands in alcoholic solution (*loc. cit.*), and it seemed of importance to discover whether under other conditions the narrow bands which had been obtained could be broken up into absorption lines, for as a vapour at atmospheric pressure iodine has very fine absorption lines, whilst in solution it gives absorption bands which are broader than those yielded by some of the polyhydroxyanthraquinone dyes. The difficulty of obtaining the absorption spectra of many organic substances as vapour is that they frequently decompose before vaporising, and hence the absorption spectra have to be observed when the dyes are vaporised at low pressures. With the same end in view, namely, of obtaining very narrow absorption bands, one of the substances, alizarin-cyanine, which gave narrow bands in alcoholic solution, was also examined in a number of organic solvents.

It may be stated here that it has not been found possible to resolve any of the bands given by the polyhydroxyanthraquinone dyes into absorption lines, but absorption curves have been obtained which on resolution into elementary symmetrical bands have yielded further information regarding the effect of the number and position of auxochromes on the absorption, and therefore on colour.

Experimental.

The absorption spectra of the dyes in concentrated sulphuric acid and of alizarin-cyanine in the various organic solvents were obtained in a manner similar to that described in the previous paper (*loc. cit.*), the apparatus being a Nutting photometer in combination with a large Hilger wave-length spectrometer. In obtaining the positions of the absorption bands in the case of the vapours, a slightly modified procedure was adopted. A brass tube 50 cm. in length and 1·5 cm. in diameter was fitted with air-tight caps taken from a polarimeter tube. The portion of these caps which is generally fixed to the glass polarimeter tube by means of hard wax was brazed to the ends of the brass tube. They were then ground plane, and by means of asbestos washers the caps could be made air-tight when screwed on firmly. Attached to the side of the brass tube was a small brass tube through which the pressure inside the long brass tube could be reduced.

To observe the absorption spectrum of the vapour of one of the dyes, a small quantity of the substance was placed in a porcelain boat and introduced into the brass tube. The polarimeter

tube cap was then firmly screwed on and the whole tube placed in a resistance electrical furnace. The latter was larger than the brass tube, and so the ends were well within the furnace. This prevented the deposition of the vaporised substance on the glass ends of the tube. The side-tube projected beyond the furnace, and was attached to a Gaede pump, by means of which the pressure inside the absorption tube could be reduced. The furnace was arranged so that a parallel beam of light could be passed through the absorption tube to one aperture of the photometer, and another beam from the same source was brought by reflections to the other aperture. This method should have given measurements from which absorption curves could have been drawn, but the difficulty of keeping the amount of vapour in the tube constant has not yet been overcome, with the result that only the wave-lengths of the maxima of absorption have been determined up to the present. Although the absorption curves have not been obtained yet for the substances in the form of vapour, an attempt has been made to classify the absorption bands according to apparent intensity. The following table contains the results which have been obtained:

TABLE I.

Substance in the form of vapour mixed with air.	Wave-lengths of maxima of absorption.	Comparative intensity of these maxima of absorption.
Quinizarin or 1 : 4-dihydroxy-anthraquinone (fluorescent)	(1) 5137	Very faint
	(2) 5040	Intense
	(3) 4926	Intense
	(4) 4815	Faint
	(5) 4736	Very faint
	(6) 4635	Extremely faint
Purpurin or 1 : 2 : 4-trihy-droxyanthraquinone	(1) 5256	Intense
	(2) 5045	Intense
	(3) Broad band of general absorp-tion from violet upwards to about 4900	Intense
Alizarin-Bordeaux or 1:2:5:8-tetrahydroxyanthraquinone	(1) 5135	Intense
	(2) 5050	Intense
	(3) 4896	Faint
	(4) 4805	Very faint
	(5) 4693	Extremely faint

These absorption bands have been shown in Figs. 2, 3, and 5 as straight lines drawn at the wave-lengths of maximum absorption and of length, varying according to the qualitative classification of intensity in the third column of Table I. It is interesting that the bands of quinizarin and Alizarin-Bordeaux vapours are closer

P P*

together than the bands of these substances in solution in alcohol, and it is also noteworthy that the differences between successive maxima of absorption of the substances as vapours are of the same order of magnitude as the differences between the successive maxima for alizarin-cyanine and anthracene-blue in alcoholic solution. The absorption due to the vapours of the other five

FIG. 1.   *Wave-lengths.*   FIG. 2.

FIG. 3.   *Wave-lengths.*   FIG. 4.

– – – – – – *Elementary symmetrical curves.*
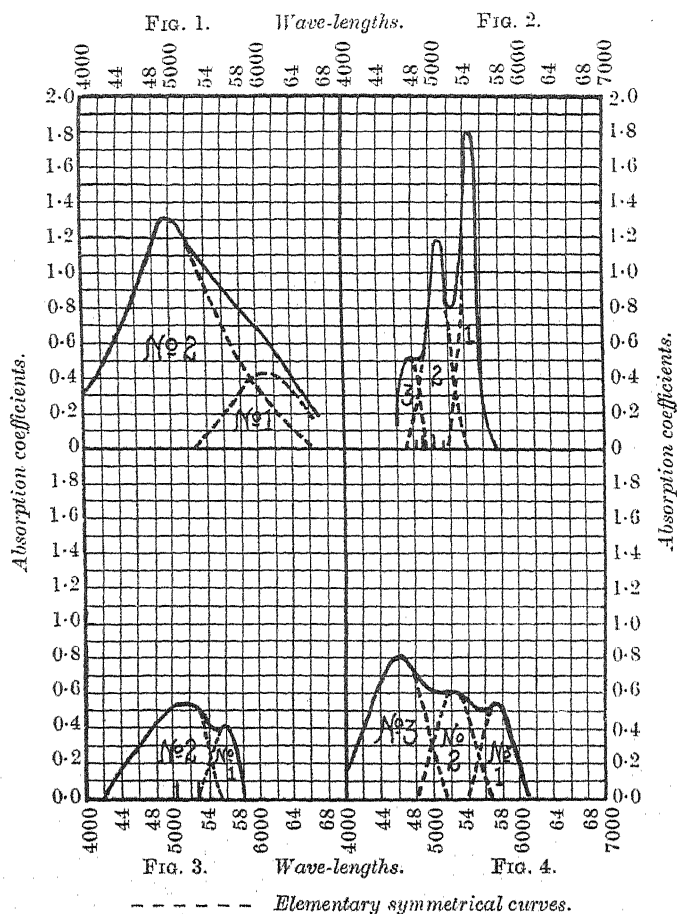
polyhydroxyanthraquinones considered here was not resolved into narrow bands. Alizarin vapour gave general absorption coming up from the violet end of the spectrum as the density of the vapour was increased. Anthragallol gave a similar result, whilst anthracene-blue gave a broad, indistinct, weak band with its centre about $\lambda = 5000$.

The Absorption Spectra of the Polyhydroxyanthraquinones in Concentrated Sulphuric Acid Solutions.

Solutions of strength $N/10^4$ in concentrated sulphuric acid were prepared and examined by the Nutting spectrophotometer in the manner previously described (*loc. cit.*). The absorption curves obtained are given in Figs. 1 to 8.

FIG. 5.   *Wave-lengths.*   FIG. 6.

FIG. 7.   *Wave-lengths.*   FIG. 8.
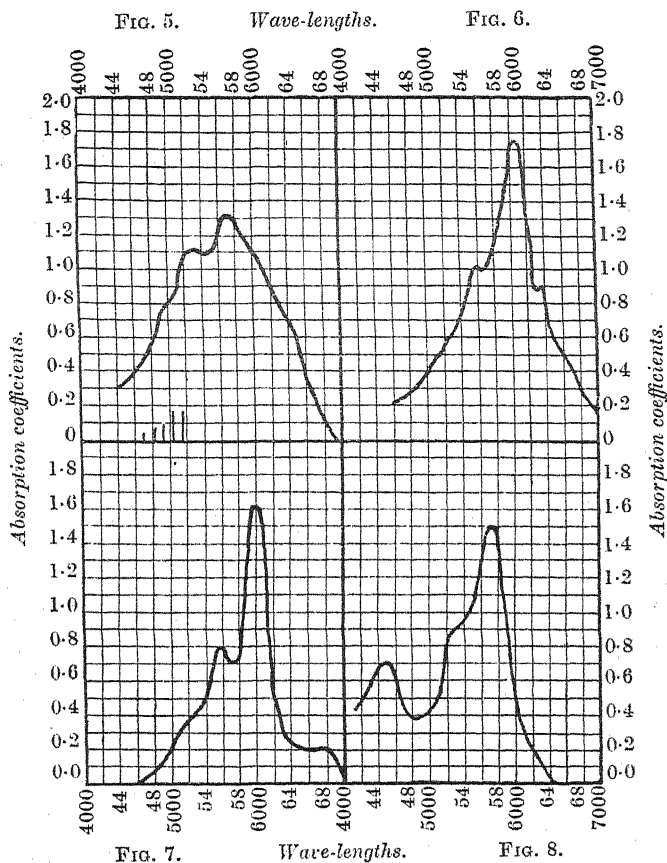
(1) *Alizarin.*—In potassium hydroxide solution there are distinctly three bands, the middle one being the most intense. In concentrated sulphuric acid solution there are indications that these bands still exist, but the middle one and the one towards the red have diminished in relative intensity, and probably also

P P* 2

have broadened.   The one towards the violet end has become relatively more intense.

(2) *Quinizarin.*—The results are given in Table II.

TABLE II.

Solvent.	Wave-lengths of maxima λ.	$f = 1/\lambda$.	$\Delta(1/\lambda)$	Relative order of intensity.	Remarks.
Vapour	(1) 5137	1946	38	—	(4)−(1)=131
	(2) 5040	1984	47	—	(5)−(2)=127
	(3) 4926	2031	46	—	(6)−(3)=127
	(4) 4815	2077	34	—	—
	(5) 4736	2111	47	—	—
	(6) 4635	2158	—	—	—
Alcohol	(1) 5150	1942	51	3	—
	(2) 5018	1993	99	2	—
	(3) 4780	2092	—	1	—
Sulphuric acid	(1) 5470	1828	139	1	—
	(2) 5086	1967	126	2	—
	(3) 4777	2093	—	3	—
Potassium hydroxide	(1) 5944	1683	127	1 ⎱ almost	—
	(2) 5526	1810	128	2 ⎰ equal	—
	(3) 5160	1938	—	3	—

The absorption spectra of quinizarin in alcohol and as a vapour have the absorption over the same area of the spectrum as regards both extent and position.   In the concentrated sulphuric acid solution and in the potassium hydroxide solution the areas of absorption are larger, but again almost equal, and they have been shifted towards the red end of the spectrum, the shift being greater in the case of the alkali solution.

(3) *Purpurin.*—The results are given in Table III.

TABLE III.

Solvent.	Wave-lengths of maxima λ.	$f = 1/\lambda$.	$\Delta(1/\lambda)$.	Relative order of intensity.	Remarks.
Vapour	(1) 5256	1903	79	(1) ⎱ about	—
	(2) 5045	1982	59?	(2) ⎰ equal	—
	(3) Broad band of general absorption from violet up to about 4900	2041?	—	—	—
Alcohol	(1) 5524	1811	110	4	—
	(2) 5205	1921	123	1	—
	(3) 4892	2044	48?	2	—
	(4) 4780?	2092?	—	3	—
Sulphuric acid	(1) 5564	1798	141	2	—
	(2) 5158	1939	—	1	—
Potassium hydroxide	(1) 5450	1835	121	2	—
	(2) 5113	1956	—	1	—

Again, in the case of purpurin, the absorptions by the vapour and by the alcoholic solutions occupy almost identical parts of the spectrum, but, as in quinizarin, the absorption maxima are closer together for the vapour than for the solution in alcohol. With concentrated sulphuric acid and potassium hydroxide solutions the absorption has been displaced towards the red, and the maxima for sulphuric acid solution are nearer the red end of the spectrum than the maxima for the alkali solution.

(4) *Anthragallol.*—In the sulphuric acid solution there are three bands giving maximum absorption at wave-lengths 5750, 5240, and 4620, and as regards intensity these are in the order 3, 2, 1 respectively. These three bands are not apparent in the potassium hydroxide solution as distinct bands, but their existence as broad bands may be inferred from the shape of the absorption curve of the potassium hydroxide solution. One effect of the sulphuric acid has been to render the resolution better and to increase the relative intensity of the absorption towards the violet end of the spectrum.

(5) *Alizarin-Bordeaux.*—The results are given in Table IV.

TABLE IV.

Solvent.	Wave-lengths of maxima λ.	$f = 1/\lambda$.	$\Delta(1/\lambda)$.	Relative order of intensity.	Remarks.
Vapour	(1) 5135	1947	33	Intense	—
	(2) 5050	1980	62	Intense	—
	(3) 4896	2042	39	Faint	—
	(4) 4805	2081	50	Very faint	—
	(5) 4693	2131	—	Extremely faint	—
Alcohol	(1) 5238?	1909?	219?	2	—
	(2) 4700	2128	—	1	—
Sulphuric acid	(1) 6400	1563	181	4	—
	(2) 5732	1744	143	1	—
	(3) 5300	1887	109	2	—
	(4) 5010	1996	—	3	—
Potassium hydroxide	(1) 6045	1655	115	2	—
	(2) 5650	1770	—	1	—

Comparing the absorption in the state of vapour and in solution in alcohol, the maximum of absorption is nearer the violet for the alcohol solution than for the vapour. In the state of vapour the bands are narrower and the resolution much better. For sulphuric acid and potassium hydroxide solutions the absorption has been displaced towards the red, and in the two solutions it occupies the same part of the spectrum. The sulphuric acid solution gives better resolution on the blue side of the absorption

curve, whereas the potassium hydroxide solution gives better resolution on the red side.

(6) *Alizarin-cyanine.*—Table V contains the results for alizarin-cyanine.

TABLE V.

Solvent.	λ for maximum.	$f = 1/\lambda.$	$\Delta(1/\lambda).$	Relative order of intensity.	Remarks.
Alcohol	(1) 5630	1776	51	3	
	(2) 5473	1827	47	1	$f - f =$
	(3) 5337	1874	92	2	(2) (4) 139
	(4) 5088	1966	43	4	
	(5) 4978	2009	89	5	
	(6) 4776	2098	—	6	
Sulphuric acid	(1) 6332	1580	76	3	
	(2) 6040	1656	137	1	$f - f =$
	(3) 5575	1793	183	2	(2) (3) 137
	(4) 5060?	1976	—	4	
Potassium hydroxide	Gradually rising curve from violet to red. No maximum between 4000 and 7000				

From table V and also from the curves it is again obvious that the absorption has been displaced towards the red in the concentrated sulphuric acid solution, and still further towards the red in the potassium hydroxide solution. The band which has been numbered (3) in the alcoholic solution has been masked in the sulphuric acid solution by the intensity of band (2), so that the bands (1), (2), (3), and (4) in sulphuric acid solution correspond with the bands (1), (2), (4), and (6) in the alcoholic solution. The band (2) in both solutions is the most intense, and it is also probable that the position of the maximum of absorption is not very much removed from the centre of the absorption band, so we may obtain the displacement towards the red in the concentrated sulphuric acid solution by comparing band number (2) in alcohol with band number (2) in sulphuric acid. These bands we may take at λ = 5473 and 6040, giving a displacement of 567 Ångström units towards red. In frequencies the figures are $f = 1827$ and 1656, with a displacement of 171.

Anthracene-blue W.R.—Table VI gives the results for anthracene-blue.

TABLE VI.

Solvent.		λ for maximum.	$f=1/\lambda$.	$\Delta(1/\lambda)$.	Relative order of intensity.	Remarks.
Alcohol	(1)	5655	1768	55	—	
	(2)	5487	1823	47	—	$f-f=$
	(3)	5348	1870	95	—	(4) (2) 142
	(4)	5089	1965	37	—	$f-f=$
	(5)	4995	2002	49	—	(5) (3) 132
	(6)	4875?	2051	—	—	
Sulphuric acid	(1)	6750?	1481	174?	—	
	(2)	6044	1655	143	—	$f-f=$
	(3)	5564	1798	129	—	(3) (2) 143
	(4)	5190	1927	—	—	
Potassium hydroxide		Gradually rising curve from violet to red with an inflection at about 5450 which shows that the curve is not a single absorption band.				

Again, the effect of the sulphuric acid and of the potassium hydroxide is to displace the absorption towards the red, and the displacement due to the sulphuric acid is not so great as that due to the potassium hydroxide. The resolution is also much better in the solution in sulphuric acid.

Alizarin-cyanine in Various Solvents.

The absorption spectra of alizarin-cyanine in various solvents have been examined, and the curves are given in Figs. 9 and 10. The results are also contained in table VII.

Alizarin-cyanine was chosen for the purpose on account of the large number of narrow bands it gives in solution in many organic solvents and the ease with which corresponding bands can be identified in the various solutions.

From Table VII, and also from Figs. 9, etc., it will be seen that the absorption bands can be recognised quite easily when displaced by the various solvents. The bands have been given distinguishing letters A, B, C, etc. The last column of Table VII contains the refractive indices of the various solvents for sodium light. According to Kundt's law, the greater the refractive index of the solvent the greater should be the displacement towards the red. This is, however, not the case. In many cases there is displacement towards the red, but this is not always accompanied by an increase in the refractive index of the solvent.

Looking at the graph of wave-lengths of maxima of absorption against refractive indices of solvents (Fig. 12), we see that, if the solvents of acid and basic nature are omitted, chloroform is the only solvent of those considered which violates Kundt's law to a

TABLE VII.

Alizarin-cyanine in Various Solvents.

Wave-lengths and frequencies of maxima of absorptions.

Solvent.		A.	B.	C.	D.	E.	F.	G.	H.	I.	J.	F—C.	Mean.	Refractive Index.
Ether	λ	—	5589	5460	5330	5214	5086	4970	4864	4761	—	—	—	1·354
	f	—	1789	1832	1876	1918	1967	2012	2056	2101	—	135	—	—
	Δf		43	44	42	49	45	44	45				44·6	—
Amyl alcohol	λ	—	5599	5483	5346	5217	5100	4992	4871	4766	4645	—	—	1·41
	f	—	1786	1824	1871	1916	1961	2003	2053	2098	2153	137	—	—
	Δf		38	47	45	45	42	50	45	55			45·9	—
Chloroform	λ	5726	5576	5432	5311	5173	5058	4960	4838	—	—	—	—	1·449
	f	1746	1793	1841	1883	1933	1977	2016	2065	—	—	136	—	—
	Δf	37	48	42	50	44	39	51					44·4	—
Acetone	λ	—	—	5458	5324	5195	5083	4962	4868	4762	4650	—	—	—
	f	—	—	1832	1879	1925	1968	2015	2055	2100	2151	136	—	—
	Δf			47	46	43	47	40	45	51			45·6	—
Methyl alcohol	λ	—	5558	5441	5313	5178	5065	4961	4847	4739	4636	—	—	1·33
	f	—	1799	1838	1882	1931	1974	2016	2063	2110	2157	136	—	—
	Δf		39	44	47	49	43	42	47	47			44·7	—

TABLE VII. (continued).

Alizarin-cyanine in Various Solvents.

Wave-lengths and frequencies of maxima of absorptions.

Solvent.		A.	B.	C.	D.	E.	F.	G.	H.	I.	J.	F—C.	Mean.	Refractive index.
Glacial acetic acid	λ	—	5568	5436	5308	5186	5058	4952	4845	4734	4628	—	—	1·37
	f	—	1796	1840	1884	1929	1977	2019	2064	2112	2161	137	—	—
	Δf		44	44	45	48	42	45	48	49				45·5	—
Pyridine	λ	—	5545	5422	5286	5159	5028	4913	4816	—	—	—	—	1·499
	f	—	1803	1844	1892	1939	1989	2036	2076	—	—	145	—	—
	Δf		41	48	47	50	47	40						45·5	—
Amyl ether	λ	5708	5608	5478	5346	5223	5102	4986	4866	4765	4665	—	—	1·418
	f	1752	1784	1827	1872	1916	1963	2008	2053	2099	2142	136	—	—
	Δf		32	43	45	44	47	45	45	46	43			44·7	—
Anisole	λ	—	5643	5512	5362	5227	5113	5000	—	—	—	—	—	1·518
	f	—	1772	1816	1865	1913	1956	2000	—	—	—	140	—	—
	Δf		44	49	48	43	44							45·6	—
Phenol	λ	—	—	5483	5375	—	5115	5005	—	—	—	—	—	1·55
	f	—	—	1822	1860	—	1956	1998	—	—	—	134	—	—
	Δf			38		96		42						—	—
Nitrobenzene	λ	1722	1772	1815	1873	1913	—	2007	2042	—	—	—	—	1·553
	f	1722	1772	1815	1873	1913	—	2007	2042	—	—	—	—	—
	Δf		50	43	58	40	94	35						—	—

large extent. Neglecting pyridine, acetic acid, and phenol, there is a general tendency to displacement towards the larger wavelength with increase of refractive index, but the nature of the

Fig. 9.
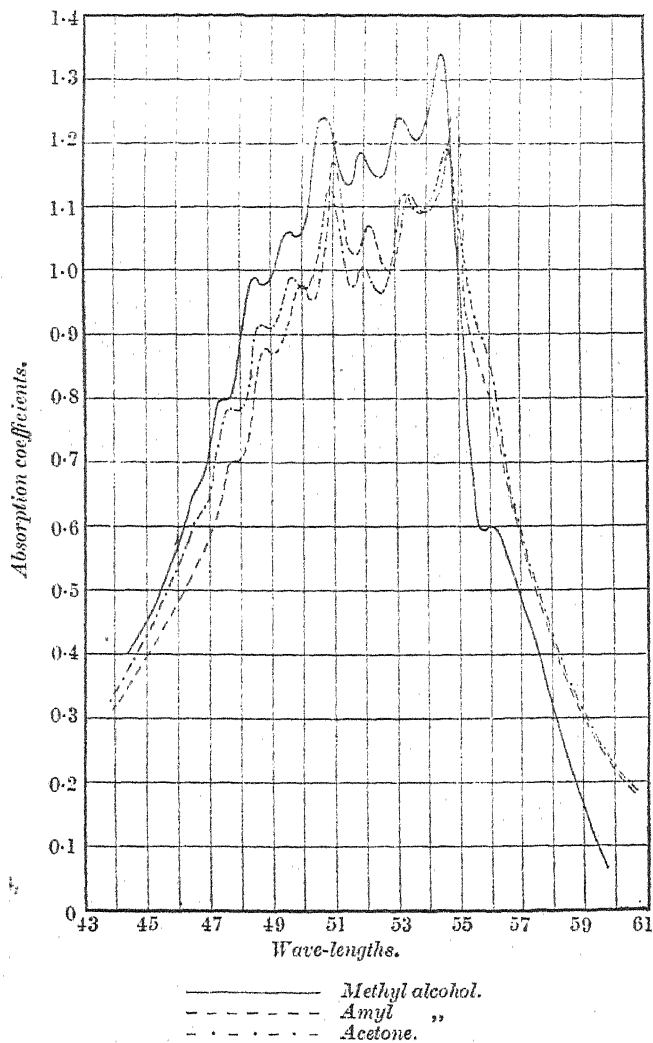
solvent as regards acidity or basicity certainly has an effect on the displacement of the absorption bands.

The displacements cannot be due to absorption bands in the

infra-red of the spectra of the solvents, for the absorption considered is that of the solution less that of the solvent.

So far as the effect of solvent on the colour of the polyhydroxyanthraquinone dyes is considered, the results are:

Fig. 10.
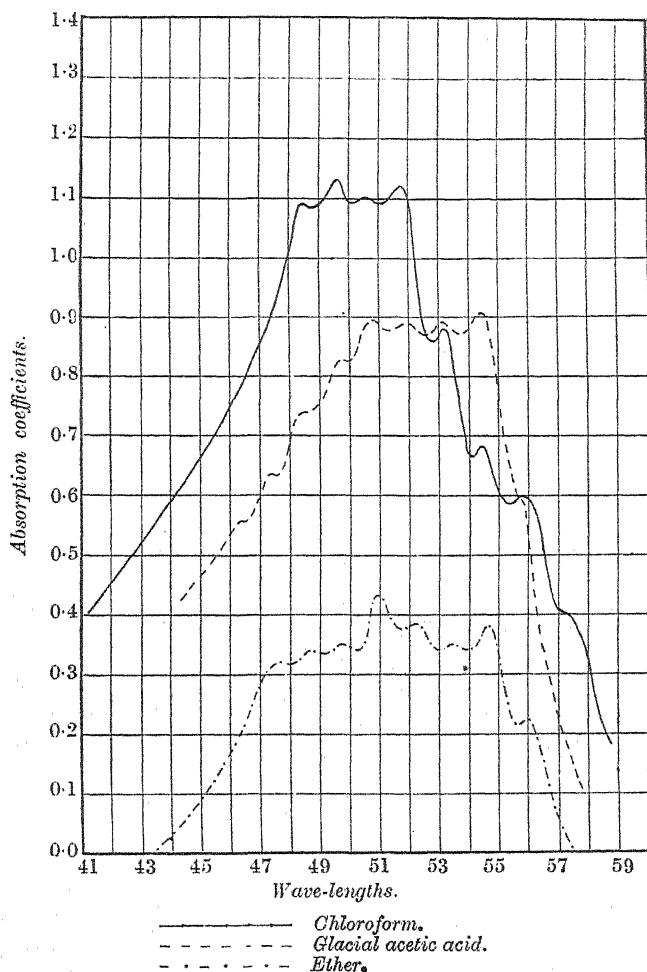
(1) The absorption is displaced towards the red end of the spectrum by solution in sulphuric acid and in potassium hydroxide as compared with absorption of the alcoholic solution.

(2) The displacement is greater for potassium hydroxide solution

than for sulphuric acid solution. The one exception is purpurin, which was shown to be an exception in other respects (T., 1916, 109, 561).

(3) The resolution in sulphuric acid solution is generally much

Fig. 11.

Alizarin-cyanine in anisole.
          ,,   ,, *pyridine.*
          ,,   ,, *phenol.*
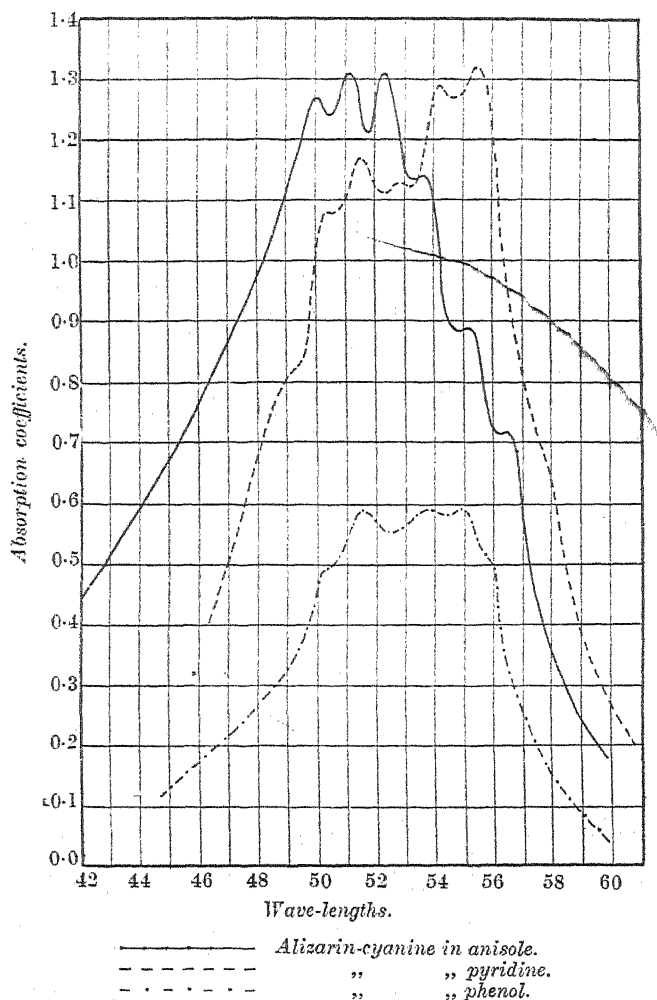
greater than in potassium hydroxide solution, and this is the case most frequently on the violet side of the group of absorption bands.

(4) For the few neutral solvents experimented with, Kundt's

law is in a general way true, but it is quite wrong when acid and basic solvents are included.

The Change in the Absorption Spectra Produced by the Variation of the Number and Position of the Auxochromes.

Previously (T., 1916, **109**, 556), the generalisations formulated by Georgievics (*Monatsh.*, 1911, **32**, 329 *et seq.*) on the influence of hydroxyl groups on the colour of lakes were criticised, and four

Fig. 12.

Wave-length of centre of same band in various solvents.
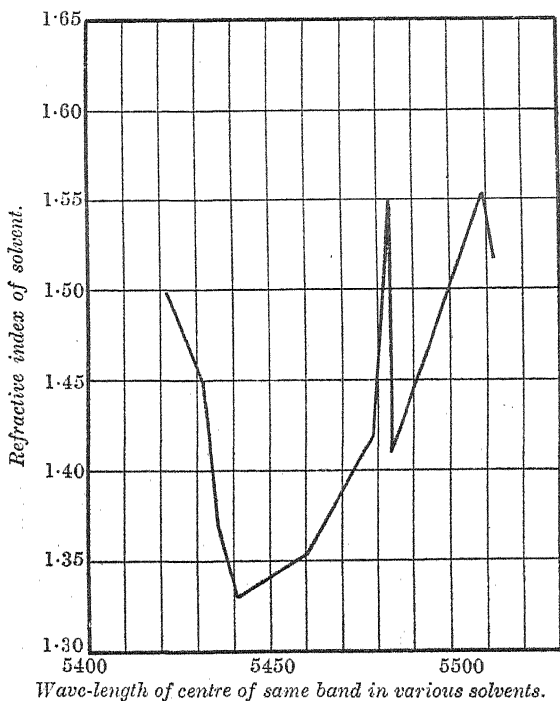
rules were formulated which seemed to be more in harmony with the facts. Pursuing this point further, the absorption curves of (1) alizarin (1:2-dihydroxyanthraquinone), (2) quinizarine (1:4-dihydroxyanthraquinone), (3) purpurin (1:2:4-trihydroxyanthraquinone), (4) anthragallol (1:2:3-trihydroxyanthraquinone) in sulphuric acid, indicated by the full lines in Figs. 1 to 4 respectively, have been resolved into symmetrical bands, shown by the dotted lines in the figures. It has frequently been suggested by various experimenters that the absorption in the visible and in

the ultra-violet portions of the spectrum is due to electrons associated with masses of various magnitudes, and calculations in the case of some substances showing selective reflection gives a mass of the order of the molecule. If we take the elementary curves in Figs. 1 to 4 and find the ratio of the values of m/pe, where m is the mass of the electron, e the charge, and p the number of electrons per molecule, for each set of elementary curves we obtain the numbers in table VIII.

TABLE VIII.

Substance.	Relative values of m/pe for elementary bands.		
	Band No. 1.	Band No. 2.	Band No. 3.
Alizarin	7	1	—
Quinizarin	1	1	3
Purpurin	2	1	—
Anthragallol	4	2	1

From Table VIII we see that the value of m/pe for the alizarin bands increases with increase in the wave-length of the maximum of absorption, whilst the reverse is the case with quinizarin. To a less degree, purpurin and anthragallol show the same effect as quinizarin and alizarin respectively. In alizarin, the hydroxyl groups are in the positions 1:2, whilst in quinizarin the groups are in the 1:4-positions. Similarly, purpurin is 1:2:4- and anthragallol is 1:2:3-trihydroxyanthraquinone. Hence from the above, and also from the curves in Figs. 1 to 4, it will be seen that the effect of the position of the auxochromes seems to be as follows: the closer the hydroxyl groups are to each other in the benzene nucleus, the broader and less intense become the bands towards the red side of the absorption group. A comparison of the curves given in the previous paper for these substances in other solvents, for example, in potassium hydroxide, bears out the same conclusion. Also it seems to be true that the proximity of the auxochromes in the benzene nucleus determines the displacement towards the red, but the mere displacement towards the red with closeness of the auxochromes becomes relatively unimportant when compared with the decrease in intensity of absorption and to the increase in the breadth of the bands on the red side of the absorption group. So far as displacement toward the longer wave-length with proximity of auxochromes is concerned, that could be explained by an increase in the period of oscillation of the electron due to an increase in the capacity of the whole system produced by the closer proximity of the auxochromes. The broadening of the bands relative to the intensity would be due to the increase

in the friction to which the absorbing vibrating electrons are subjected, for if we take a simple absorption band produced by electrons moving according to the equation

$$m \frac{d^2x}{dt^2} + k \frac{dx}{dt} + n^2x = E \cos ft.$$

then the term $k \frac{dx}{dt}$ represents the allowance made for friction, and the greater the value of k the greater the breadth of the absorption band relative to its intensity, that is, the greater the friction the broader the absorption bands.

The results, then, of bringing the auxochromes close together in the benzene nucleus are:

(1) A displacement of the absorption · bands towards longer wave-lengths, and

(2) A decrease of the intensity of the bands relative to their breadth.

The latter result produces a greater change on the colour than the former. It is responsible for the brown colour of such dyes as anthragallol and rufigallol in certain solvents.

The Absorption Spectrum of Alizarin-Cyanine in Piperidine.

When a solution of strength $N/10^4$ was prepared, 1 cm. thickness gave the absorption curve (1) in Fig. 13 half an hour after preparation. Taking the wave-length where the absorption is a maximum as the centre of an absorption band, then curve (1) in Fig. 13 gives the bands tabulated in table IX.

TABLE IX.

Band.	A.	B.	C.	D.	E.	F.	G.
Wave-length	5990	5757	5544	5442	5295	5153	5064
Intensity	0·48	0·526	0·64	0·613	0·50	0·434	0·354
Relative order of intensity	5	3	1	2	4	6	7

The absorption changes while the observations are being taken, so that time readings are necessary to obtain the absorption curve at a definite time after the preparation of the solution. Examination of the solution immediately it has been prepared shows that the bands A, B, and E are absent, or at least very faint, and that with time they begin to appear. When the solution is freshly prepared, C is the most intense band, and next in intensity comes D. The solution was allowed to remain in the dark for forty-even hours, and the absorption curve was then (2) of Fig. 13. The vessel remained sealed throughout the experiments from the

moment when the alizarin-cyanine was added to the piperidine,
and therefore water vapour and carbon dioxide were excluded.)

FIG. 13.
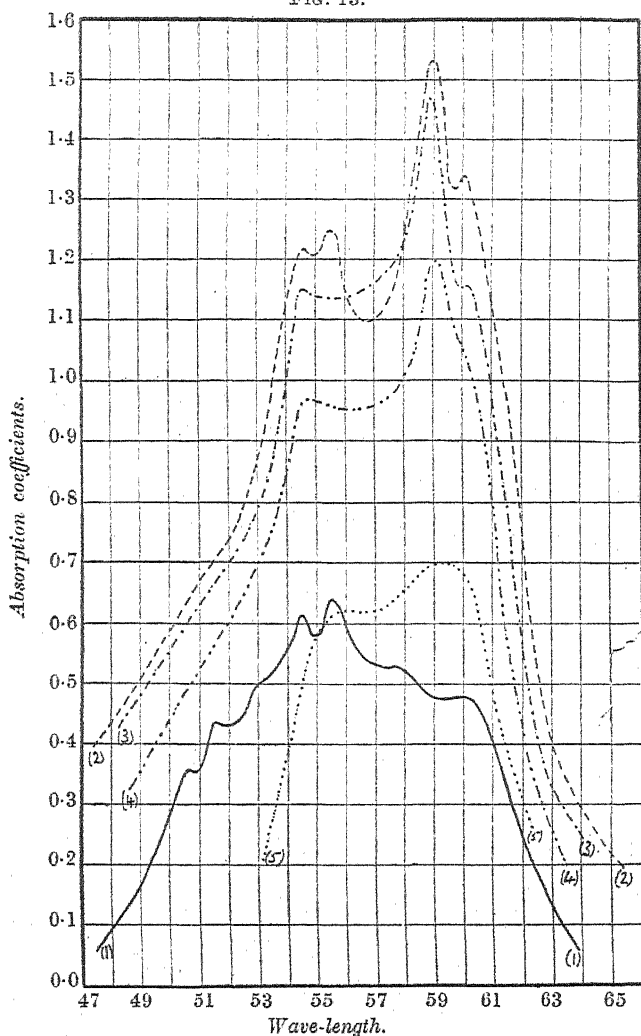
(1) *Alizarin-cyanine in piperidine* ½ *hour after preparation.*
(2)   ,,   ,,   ,,   47 *hours* ,,   ,,
(3)   ,,   ,,   ,,   71   ,,   ,,   ,,
(4)   ,,   ,,   ,,   95   ,,   ,,   ,,
(5)   ,,   ,, *ammonia.*

The same bands are still present, but E, F, and G are only show
by a change in the gradient of the curve. The intensity of ℓ

the bands has increased, and A and B have increased to a greater degree than C and D, with the result that B is now the band of maximum intensity.   The wave-lengths corresponding with the maxima of A and B have increased.   That need not be considered as due to any shift of the bands, but merely as the natural displacement of the maxima caused by the change in the relative intensities of the A and B bands with respect to the C and D bands.   Curve (3), Fig. 13, gives the absorption of the same thickness of the same solution seventy-one hours after preparation. The intensity of absorption throughout has decreased.   The bands A and B still remain distinguishable, but C and D have become merged into one band.   After ninety-five hours from preparation the same solution has only two bands remaining, namely, B and D, with a slight suggestion of A.   The intensity has decreased further and the fading continues.   The wave-lengths of maxima of absorption are now 5902 and 5454, and comparing the absorption curve (4) with the curve for alizarin-cyanine in concentrated ammonia solution (5), a strong resemblance is observed.

Fading of the solution, or, what is the same thing, general decrease in intensity of the absorption throughout, must be explained by a decrease per unit volume of the number of vibrating systems giving the various bands, but the disappearance from the absorption curve of the individual bands A, C, E, F, and G can only be explained by a broadening of these bands.   This, on the ordinary mechanical theory, would mean that the frictional element in the forced vibrations causing these bands was increased, and that therefore systems with periods differing from the true natural period by large amounts are made to resonate.   It is not assumed that the individual bands A, C, E, F, and G have disappeared entirely, but they have broadened to such a degree that the observed curve does not show them resolved as separate bands.

The conclusion drawn previously (T., 1916, **109**, 555), that "the more electropositive the nature of the radicle attached to the conjugate chain the longer will be the wave-length of the maximum of the absorption band," is supported by the comparison of the absorption curves of alizarin-cyanine in alcohol and in piperidine.   In this case, the absorption curve of the solution in piperidine shows an intensification of the bands toward the longer wave-length and a diminution of the intensity of the bands towards the shorter wave-length.   With the solution in potassium hydroxide, and the dyed fabrics on chrome, alum, and tin mordants, the absorption curves were broad and did not show the separate bands as such.   This would mean that the friction is much greater on these mordanted fabrics and also in the potassium hydroxide

solution than in the alcoholic solution, and the displacement of
the centre of the broad resultant band would then be given by
the increase of the intensity of the elementary bands towards the
red end of the spectrum when the electropositive nature of the
radicle is increased.

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LXXXIV.—*Action of Phenylhydrazine on Opianic, Nitro-opianic, and Phthalonic Acids: Some Derivatives of Hydrazo- and Azo-phthalide.*

By Prafulla Chandra Mitter and Jnanendra Nath Sen.

The action of phenylhydrazine on opianic and nitro-opianic acids
was first studied by Liebermann (*Ber.*, 1886, **19**, 763), who found
that in the case of opianic acid one molecule of the acid reacts
with one molecule of phenylhydrazine, with the elimination of two
molecules of water and the formation of a compound insoluble in
alkalis, to which he attributed a ring structure.

In the case of nitro-opianic acid, an intermediate product soluble
in alkalis, which therefore was regarded as the ordinary phenyl-
hydrazine derivative of nitro-opianic acid, was isolated. This sub-
stance could be purified by dissolving in cold acetone and pre-
cipitation with water. On recrystallisation from glacial acetic
acid, however, it was converted into a compound insoluble in
alkalis and containing one molecule of water less than the phenyl-
hydrazine derivative, and to this compound too a ring structure
was assigned.

A behaviour similar to that of opianic acid on treatment with
phenylhydrazine had been observed by Roser in the case of a
number of *o*-keto-carboxylic acids (*Ber.*, 1885, **18**, 802). In every
case, from one molecule of keto-acid and one molecule of phenyl-
hydrazine two molecules of water instead of one were eliminated,
with the formation of ring compounds. Intermediate phenyl-
hydrazine derivatives formed by the primary action of phenyl-
hydrazine on the aldehydo-group could not be obtained.

For the preparation of these compounds, Roser heated the sub-
stances in alcoholic solution with phenylhydrazine and acetic acid,

whilst Liebermann treated the substances in aqueous solution with phenylhydrazine hydrochloride and sodium acetate. In both cases the reaction took place in the presence of acetic acid.

It has been found that in ethereal solution and with the free base the reaction takes place in a novel manner, with the loss of only one molecule of water. The products can in some cases be crystallised from dilute acetone. They vary in their degree of stability, and in some cases remain unchanged for days, especially during the cold season.

On treatment with acetic acid, the substances are instantaneously converted, by loss of a further molecule of water, into ring compounds identical with those obtained by Liebermann and others.

For the phenylhydrazine derivative (for example, from opianic acid) we have the choice of two alternative formulæ,

$$MeO \underset{MeO}{\overset{}{\bigcirc}} \begin{array}{l} CH\!:\!N\!\cdot\!NHPh \\ CO_2H \end{array} \quad and \quad MeO \underset{MeO}{\overset{}{\bigcirc}} \begin{array}{l} CH(NH\!\cdot\!NHPh) \\ CO \end{array}\!\!\!>\!O$$

$$(I.) \qquad\qquad\qquad (II.)$$
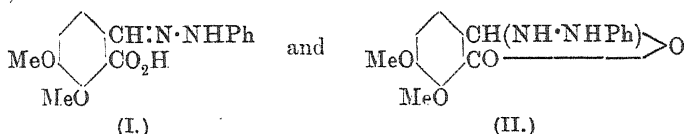
We are in favour of formula II, because on subsequent oxidation with mercuric oxide in acetone solution, the phenylhydrazine derivatives are converted into deep-coloured substances which give all the usual reactions of azo-compounds. The formation of an azo-compound by oxidation is a definite indication in favour of the hydrazo-structure. With the ordinary formula, such a change cannot be explained without assuming a considerable amount of molecular rearrangement and redistribution of linkings.

The azophthalides which have been prepared in this way represent an altogether new class of azo-compounds.

The mechanism of the reaction in this case, and in the case of amines generally, appears to be as follows. The elimination of water takes place, in the first instance, between the aldehydo-group on the one hand and the amino- or imino-group on the other. The hydrogen atom of the carboxyl group subsequently oscillates to the nitrogen, forming a phthalide ring.

In the case of a primary amine, the change may be represented thus:

$$\overset{}{\bigcirc} \begin{array}{l} CH\!:\!NR \\ CO_2H \end{array} \quad \longrightarrow \quad \overset{}{\bigcirc} \begin{array}{l} CH(NHR) \\ CO \end{array}\!\!\!>\!O.$$
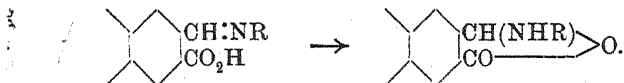
In the case of secondary amines, two molecules of the amine react with one molecule of the aldehyde, and when the hydrogen atom of the carboxyl group oscillates to the nitrogen atom, a molecule

of the amine is regenerated, which is at once detached from the condensation product, thus:

$$\text{(ring)}\begin{array}{l}\text{CH(NRR')}_2\\\text{CO}_2\text{H}\end{array} \longrightarrow \text{(ring)}\begin{array}{l}\text{CH(NRR')}\\\text{CO}\end{array}\!\!>\!\text{O} + \text{NHRR'}.$$
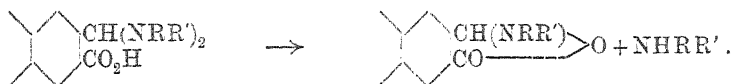
In the case of phenylhydrazine the action is exactly similar, thus:

$$\text{(ring)}\begin{array}{l}\text{CH:N·NHPh}\\\text{CO}_2\text{H}\end{array} \longrightarrow \text{(ring)}\begin{array}{l}\text{CH(NH·NHPh)}\\\text{CO}\end{array}\!\!>\!\text{O}.$$
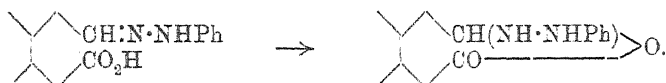
The formation of stable azo-compounds by oxidation would thus be readily explained, and they would have the structure represented below:

$$\text{(ring)}\begin{array}{l}\text{CH(NH·NHPh)}\\\text{CO}\end{array}\!\!>\!\text{O} \longrightarrow \text{(ring)}\begin{array}{l}\text{CH(N:NPh)}\\\text{CO}\end{array}\!\!>\!\text{O}.$$
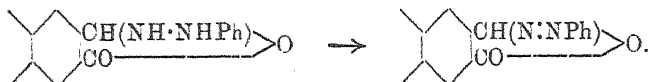
The oscillating hydrogen atom can, of course, revert at any moment to the original position, which it apparently does in acid and alkaline media. This explains the solubility of the substance in alkalis, as well as the formation of the phthalazone ring under the dehydrating influence of different acids.

On oxidation to the azo-compounds, the hydrogen atom is removed, with the result that the products become insoluble in alkalis, unlike the hydrazo-compounds.

Such oscillation of hydrogen of the carboxyl group to doubly or trebly linked atoms or radicles in the *o*-position with respect to the carboxyl group is not without many parallels.

EXPERIMENTAL.

Interaction of Phenylhydrazine and Opianic Acid.

Opianic acid is rather sparingly soluble in ether, but on adding the acid to an ethereal solution of phenylhydrazine it dissolves readily. The solution on keeping deposits minute crystals of the phenylhydrazine derivative.

Five grams of phenylhydrazine hydrochloride were treated with sodium hydroxide, and to the ethereal solution of the liberated base 5 grams of opianic acid were gradually added with constant stirring, the vessel being kept cool with ice-water. The acid dissolved, and on scratching the sides of the vessel minute crystals soon appeared. To ensure completion of the reaction, the mixture was allowed to remain for about half an hour. The precipitate was washed repeatedly with ether and then dried in the air. The yield was 5·5 grams.

The substance crystallises from dilute acetone in pale pink needles melting and decomposing at 146°. It is soluble not only in dilute alkali carbonate, but also in dilute sodium hydroxide and ammonia, and less readily so in sodium hydrogen carbonate. In the cold it does not dissolve in hydrochloric acid, but on warming solution takes place. Concentrated nitric acid dissolves it immediately, with the evolution of nitrous fumes and the production of a deep red colour. With concentrated sulphuric acid, it gives no colour. Acetic acid transforms it into the ring compound:

0·1454 gave 0·3413 CO_2 and 0·0786 H_2O. C = 64·02; H = 6·01.

0·0996 ,, 7·9 c.c. N_2 at 21·5° and 760 mm. N = 9·19.

$C_{16}H_{16}O_4N_2$ requires C = 64·00; H = 5·33; N = 9·33 per cent.

The substance was dissolved in dilute standard alkali and the excess of alkali titrated with standard oxalic acid. It was found to be monobasic.

0·1889 required 6·4 c.c. $N/10$-acid, whilst this weight of a monobasic acid of the above formula requires 6·28 c.c. $N/10$-acid.

Phenylazomeconin.

One gram of phenylhydrazomeconin (formula II) was dissolved in 25 c.c. of pure acetone (free from methyl alcohol) and heated on the water-bath with 4 grams of red mercuric oxide, the liquid being kept almost at boiling point. The colour of the solution gradually changed to crimson-red. After remaining overnight, the mixture was filtered and the filtrate allowed to evaporate in the air, when a pasty mass was left which became hard on treatment with ether. The substance was dissolved in acetone and ether added to the solution. A pale yellow, flocculent precipitate was formed which had a tendency to become tarry, and, after removing this by filtration, the filtrate was allowed to evaporate in a vacuum over sulphuric acid. A residue was left which, after crystallisation from dilute acetic acid, was obtained as a yellow, crystalline powder melting at 164°.

Phenylazomeconin gives all the usual reactions of an azo-compound. With concentrated sulphuric acid it gives a violet colour. The colour of the substance itself is discharged by treatment with a solution of stannous chloride and hydrochloric acid. It dissolves in glacial acetic acid with a red colour, which intensifies on warming. If to this solution zinc dust is added and the whole heated for a moment, the colour changes to pale yellow, with the formation of a precipitate. In alcohol, it dissolves with a pink colour, which deepens on the addition of alkalis. It is readily soluble in acetone, chloroform, or benzene:

0·1034 gave 0·2438 CO_2 and 0·0449 H_2O. C = 64·34 ; H = 4·82.
0·1003 „ 8·4 c.c. N_2 at 25° and 760 mm. N = 9·59.
$C_{16}H_{14}O_4N_2$ requires C = 64·43 ; H = 4·69 ; N = 9·39 per cent.

Phenylopiazone.

One gram of phenylhydrazomeconin was dissolved in hot glacial acetic acid, the solution boiled for about five minutes, and water added, when the ring compound was precipitated in almost colourless flakes. It was purified by redissolving it in dilute acetic acid and boiling with animal charcoal. On filtration and cooling, crystals separated which were perfectly transparent and melted sharply at 175°. (Found : C = 68·62 ; H = 5·26. $C_{16}H_{14}O_3N_2$ requires C = 68·08 ; H = 4·96 per cent.) This substance is identical with the opianylphenylhydrazide described by Liebermann.

It is insoluble in alkalis or alkali carbonates and does not develop any colour with concentrated sulphuric or nitric acids.

Interaction of Phenylhydrazine and Nitro-opianic Acid.

To an ethereal solution of phenylhydrazine (from 1·5 grams of the hydrochloride) 1 gram of nitro-opianic acid was gradually added. In a few minutes, after solution was complete, a red oil settled to the bottom, which, on stirring, solidified to a crystalline mass, which was collected and washed with ether. It crystallised from dilute acetone in red needles melting at 184° (Found : N = 12·26. $C_{16}H_{15}O_6N_3$ requires N = 12·17 per cent.), evidently identical with Liebermann's "nitro-opianic acid phenylhydrazine." The substance is soluble in alkalis or alkali carbonates. With sulphuric acid it gives but a pale green colour.

Phenylazonitromeconin.

Phenylhydrazonitromeconin (0·8 gram) was dissolved in 15 c.c. of pure acetone, and 1·5 grams of red mercuric oxide were added. The liquid was kept gently boiling on a water-bath under reflux for about two hours, after which it was left at the ordinary temperature for twenty-four hours. The mixture was then filtered, the residue repeatedly extracted with boiling acetone, and the acetone solution evaporated, when a brick-red, crystalline mass was obtained. This was treated with excess of sodium carbonate to remove any trace of the hydrazo-compound, thoroughly washed with water, and crystallised from dilute acetone, from which it

separated as an orange, crystalline powder melting sharply at 217°. The substance is sparingly soluble in acetone and insoluble in all other common solvents. With concentrated sulphuric acid it gives a blue colour:

0·0959 gave 0·1976 CO_2 and 0·0286 H_2O. C=56·19; H=3·32.
0·1632 ,, 17 c.c. N_2 at 20° and 760·01 mm. N=12·14.
$C_{16}H_{13}O_6N_3$ requires C=55·97; H=3·79; N=12·26 per cent.

Interaction of Phenylhydrazine and Phthalonic Acid.

With phthalonic acid and phenylhydrazine an intermediate hydrazo-compound was obtained which could be oxidised to the corresponding azo-compound by means of mercuric oxide in acetone solution. It was also converted into the corresponding ring compound by dehydration with acetic acid. The hydrazo- and azo-compounds have not, however, been obtained in a condition sufficiently pure for analysis.

Phenylphthalazonecarboxylic Acid,
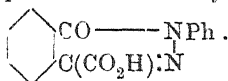
One gram of phenylhydrazophthalidecarboxylic acid was dissolved in warm glacial acetic acid and hot water added to the solution. On cooling, crystals of the ring compound were obtained in matted needles melting at 208°. The substance is identical with the anhydrophenylhydrazine-*o*-carboxyphenylglyoxylic acid prepared by Henriques (*Ber.*, 1888, **21**, 1610).

Further investigations are in progress.

Sir T. N. Palit Laboratory,
    College of Science,
        University of Calcutta.   (*Received, June 18th*, 1917.]

LXXXV.—*Studies of the Carbonates. Part III. Lithium, Calcium, and Magnesium Carbonates.*

By CLARENCE ARTHUR SEYLER and PERCY VIVIAN LLOYD.

Lithium Carbonate.

AIR was drawn through an $N/10$-solution of lithium hydrogen carbonate at 25°. The percentage of carbonic acid in the air was determined as in the previous paper (this vol., p. 138), by drawing air through an $N/10$-solution of sodium carbonate.

$c = 100 \cdot 5 \times 10^{-3}$ gram-equivalents per litre $[H_2CO_3] = 0 \cdot 0105 \times 10^{-3}$.

$100x =$ hydrogen carbonate 40·65 per cent.

$100(1 - x) =$ carbonate 59·35 per cent.

This result is identical within the limits of experimental error with that for sodium carbonate at the same concentration, and gives $\dfrac{k_2}{k_3} \dfrac{\beta}{a^2} = 5326$.

Air was drawn through water containing lithium carbonate in excess. $c = 363 \times 10^{-3}$ equivalents.

$100x =$ hydrogen carbonate 23·4 per cent. $\left.\right\}$

$100(1 - x) =$ carbonate 76·6 per cent. $\left.\right\}$ $\dfrac{k_2}{k_3} \dfrac{\beta}{a^2} = 4272$.

This result agrees with McCoy's value for sodium carbonate at the same concentration.

Lithium carbonate, when shaken with water alone ($c = 338 \times 10^{-3}$), behaved analytically like a pure carbonate. It is evident, therefore, that the ionisation of lithium carbonate and hydrogen carbonate can be taken as equal to that of sodium carbonate and hydrogen carbonate.

A series of experiments was made, the results of which, although only preliminary, are worth recording. Lithium carbonate was shaken with water containing increasing amounts of carbonic acid in bottles without air space until equilibrium was presumed to be reached. The proportion of carbonate and hydrogen carbonate to total base was ascertained by double titration without special precautions, except against loss of carbonic acid. The solid phase, even when the solution contained chiefly hydrogen carbonate, appeared to be lithium carbonate, as determined by dissolving a portion in pure water and titrating as above. The concentration of the free carbonic acid was not determined, but can be approximately calculated by the equation $[H_2CO_3] = \dfrac{k_3}{k_2} \cdot \dfrac{[HCO_3]^2}{[CO_3]}$ and is

small in any case. The object was to ascertain whether the solubility product $[Li]^2 \times [CO_3]$ was approximately constant. Such experiments would afford a criterion as to whether the intermediate ion $LiCO_3$ really exists, since if it does the lithium ion concentration will be $[HCO_3] + [LiCO_3] + 2[CO_3]$, whilst if it does not, it will be $[HCO_3] + 2[CO_3]$.

If b is the molecular concentration of the total hydrogen carbonate and c that of the carbonate, as determined by analysis, we should have in the first case $[Li] = a(b + c) + \beta c$, and in the second $[Li'] = ab + 2\beta c$; β is taken to be the same as for sodium carbonate at the same total lithium concentration and a to be the same as for sodium acetate at the same molecular concentration, that is, at the concentration $b + c$. The non-ionised $[Li_2CO_3]$ will be $(1 - a)b$ and the $[LiCO_3] = c(a - \beta)$.

Equivalent concentration.					
$b + 2c$.	$b + c$.	b.	a.	$[HCO_3]$.	c.
338×10^{-3}	169×10^{-3}	0	0·75	0×10^{-3}	169×10^{-3}
363	224	85	0·72	61·0	139
364	215	66	0·72	47·5	149
386	248	110	0·71	78·1	138
406	282	158	0·70	110·6	124
706	635	570	0·595	339·0	65
818	773	728	0·56	407·7	45

β.	$[CO_3]$.	$[Li]$.	$[Li']$.	$[Li] \times {}^2[CO_3]$.	$[Li'] \times {}^2[CO_3]$.
0·295	$49·85 \times 10^{-3}$	$176·5 \times 10^{-3}$	$99·7 \times 10^{-3}$	$1·553 \times 10^{-3}$	$0·495 \times 10^{-3}$
0·285	39·60	200·9	140·4	1·598	0·780
0·285	42·50	197·3	132·5	1·654	0·740
0·275	37·9	214·0	153·9	1·736	0·89
0·267	33·2	230·6	177·0	1·765	1·04
0·187	12·1	389·9	363·2	1·84	1·59
0·165	7·42	441·2	422·5	1·46	1·32

On the assumption of an intermediate ion, the value of $[Li]^2 \times [CO_3]$ is fairly constant, whereas on the other assumption there is no constancy until the effect of the intermediate ion becomes negligible. It will be found that although $[Li]^2 \times [CO_3]$ is approximately constant, the non-ionised $[Li_2CO_3]$ diminishes, so that $\dfrac{[Li]^2 \times [CO_3]}{[Li_2CO_3]} = k_a k_b$ increases. Since $\dfrac{[Li] \times [CO_3]}{[LiCO_3]} = k_b$ is roughly constant* (see this vol., p. 143), it follows that the product $[Li] \times [LiCO_3]$ must also be approximately constant. It seems, therefore, that it is the non-ionised molecule that does not follow the law of mass action, or of which the concentration is not a true measure of the active mass. These experiments indicate a line of research which is worth pursuing by experiments in which all the conditions are accurately controlled.

* k_b increases with the concentration, but much less rapidly than k_a.

Calcium Carbonate.

Stieglitz (*Carnegie Institution Pub.*, 1909, No. 107) and McCoy and Smith (*J. Amer. Chem. Soc.*, 1911, **33**, 468) have calculated the solubility product $[Ca] \times [CO_3] = k_1$ of calcium carbonate from the value of $2\dfrac{k_2}{k_3}[Ca] \times [CO_3]$ obtained by Schlœsing (or by McCoy and Smith).

Stieglitz used the value $k_3 = 6 \cdot 2 \times 10^{-11}$ and McCoy and Smith $5 \cdot 5 \times 10^{-11}$.

It has been shown (Part II., *loc. cit.*) that these values are probably too high. We found the values $k_3 = 4 \cdot 27 \times 10^{-11}$, $\dfrac{k_2}{k_3} = 7124$ and $\dfrac{k_w}{k_3} = 19 \cdot 2 \times 10^{-5}$. Consequently, the value of $[Ca] \times [CO_3] = k_1$ obtained by Stieglitz and by McCoy and Smith is too high. Taking the result of McCoy and Smith's experiments, we have $2\dfrac{k_2}{k_3}k_1 = 102 \cdot 5 \times 10^{-6}$, whence $[Ca] \times [CO_3] = k_1 = 71 \cdot 9 \times 10^{-10}$ at 25°.

McCoy and Smith calculated it to be 93×10^{-10} and Stieglitz 126×10^{-10}.

This high result explains why the calculations of the solubility of calcium carbonate in pure water have hitherto been materially larger than the value found by experiment.

McCoy and Smith, for instance, calculated it to be $16 \cdot 6 \times 10^{-5}$ gram-molecules per litre at 25°, whilst Kendall (*Phil. Mag.*, 1912, [vi], **23**, 958) found only $14 \cdot 33 \times 10^{-5}$.

We recalculate it on a basis of $[Ca] \times [CO_3] = 71 \cdot 9 \times 10^{-10}$, as follows : The pure calcium carbonate is largely hydrolysed at this dilution, thus:

$$CaCO_3 + 2H_2O = Ca(OH)_2 + Ca(HCO_3)_2,$$
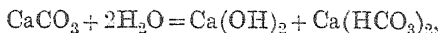
where the concentration $[HCO_3] = [OH]$. Therefore

$$[Ca] = [CO_3] + \frac{[HCO_3]}{2} + \frac{[OH]}{2} = [CO_3] + [HCO_3].$$

Also

$$\frac{[HCO_3] \times [OH]}{[CO_3]} = \frac{k_w}{k_3} = \frac{[HCO_3]^2}{[CO_3]}.$$

If $100x$ is the percentage of the calcium carbonate hydrolysed, $[HCO_3] = x[Ca]$, $[CO_3] = (1-x)[Ca]$,

$$\frac{x^2}{1-x}[Ca] = \frac{k_w}{k_3} = 1 \cdot 92 \times 10^{-4}.$$

But $[Ca] \times [CO_3] = [Ca]^2(1-x) = 71 \cdot 9 \times 10^{-10}$.

We have two equations for [Ca] and x which are satisfied by a] $= 14\cdot6 \times 10^{-5}$ and $x = 0\cdot666$; that is to say, the solubility of calcium carbonate will be $14\cdot6 \times 10^{-5}$ gram-molecules per litre, of which two-thirds will be hydrolysed. The alteration of $\dfrac{k_w}{k_3}$ to $1\cdot67 \times 10^{-4}$ will make very little change. [Ca] will become $14\cdot24 \times 10^{-5}$ and $x = 0\cdot645$.

The solubility of calcium carbonate, using normal air, can also be calculated:

$$\frac{[HCO_3]^2}{[CO_3].[H_2CO_3]} = 7124 \quad [Ca] \times [CO_3] = 71\cdot9 \times 10^{-10} \quad [HCO_3] = 2([Ca] - [CO_3]).$$

Therefore,

$$\frac{([Ca] - [CO_3])^2}{[CO_3]} = \frac{7124}{4}[H_2CO_3].$$

For air containing $0\cdot037$ per cent. of carbon dioxide $[H_2CO_3]$ at $25°$ will be $1\cdot221 \times 10^{-5}$. This will give $[a] = 54\cdot7 \times 10^{-5}$, but Kendall found considerably less. His result appears to be low. In an experiment conducted at about $15°$ it was found that after twenty-eight days the solubility of powdered limestone suspended in water through which air from outside the laboratory was drawn was $33\cdot7 \times 10^{-5}$. After sixty-nine days it rose to $54\cdot2 \times 10^{-5}$, and after two hundred and forty days to $57\cdot5 \times 10^{-5}$, so that equilibrium is only slowly reached.

Assuming $0\cdot033$ per cent. of carbon dioxide in the air, $[H_2CO_3]$ at $15° = 1\cdot475 \times 10^{-5}$. This will give $[a] = 58\cdot2 \times 10^{-5}$, against $57\cdot5 \times 10^{-5}$ found.

For air containing $0\cdot0333$ per cent. of carbon dioxide, Schloesing found (at $18°$) $54\cdot88 \times 10^{-3}$.

The solution of the carbonate in equilibrium with air was found to have a slightly alkaline reaction to phenolphthalein. (For a full discussion of the subject, see Johnston and Williamson, *J. Amer. Chem. Soc.*, 1916, **38**, 975.)

Magnesium Carbonate.

Bodländer has calculated the ratio

$$\frac{[Mg] \times [HCO_3]^2}{[H_2CO_3]} = \frac{k_2}{k_3}[Mg] \times [CO_3].$$

from Engel's experiments on the solubility of crystallised magnesium carbonate, $MgCO_3,3H_2O$, in water containing carbonic acid under pressures of from $\frac{1}{2}$ to 6 atmospheres. At these tensions the carbonate is a stable solid phase. The difficulty presents itself that the carbonate, unlike calcium, barium, or strontium carbon-

ates, is not sparingly soluble. Engel states that it is soluble in
water to the extent of $11·5 \times 10^{-3}$ gram-molecules per litre at 12·
and Bodländer assumes that 56 per cent. is dissociated, giving a
concentration of $5·06 \times 10^{-3}$ for the non-ionised part, which Bod-
länder deducts in calculating the concentration of the magnesium
and hydrogen carbonate. However, this is erroneous. Crystallised
magnesium carbonate has no definite solubility in pure water. It
is decomposed into basic compounds, and the solution contains
magnesium hydrogen carbonate with a certain amount of ionised
and non-ionised carbonate.

The magnesium in solution depends on the ratio of water to solid
employed, and the equilibrium takes some time to reach completion.
The following results bearing on this question were obtained. The
total carbonic acid was determined by Dittmar's ' vacuum method '
(" Quantitative Chemical Analysis," p. 227) used by him for sea-
water, the ' fixed ' carbonic acid by titration with methyl-orange as
indicator :

Time (days).	Water / Solid.	$\dfrac{C_{Mg}}{2}$	$\dfrac{C_{Mg(HCO_3)_2}}{2}$	C_{MgCO_3}.	$\dfrac{[CO_2]}{[MgO]}$. in solid.	$[H_2CO_3]$.
440	unknown	$5·98 \times 10^{-3}$	$1·58 \times 10^{-3}$	$2·20 \times 10^{-3}$	0·775	
440	370	8·48	3·48	2·50	0·772	
—		15·96	10·21	2·87	—	$0·0103 \times 10^{-3}$
335	unknown	31·0	22·15	4·57	0·79	
47	17	47·5	34·1	6·70	0·84	
338	unknown	48·9	33·9	7·50	—	
47	8·5	60·0	46·6	6·70	0·79	
47	2·0	76·62	63·5	6·56	0·79	

The subject deserves careful investigation, but it is evident that
the carbonate below a certain tension of carbonic acid is decom-
posed until the solid phase is not far removed from hydromag-·
nesite, $3MgCO_3,Mg(OH)_2,3H_2O$ $\left(\text{ratio, } \dfrac{[CO_2]}{[MgO]} = 0·75\right)$, which is,
stable over a fairly wide range of concentration of carbonic acid.
The magnesium remains in solution largely as hydrogen carbonate,
with a proportion of carbonate both ionised and non-ionised. The
main reaction is approximately

$$5MgCO_3 + 2H_2O = 3MgCO_3,Mg(OH)_2 + Mg(HCO_3)_2.$$
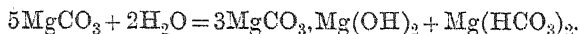
Consequently, the greater the amount of magnesium carbonate in
relation to the water the greater is the concentration of the solu-
tion. The dissolved carbonate with increasing concentration (and
when sufficient time is allowed) becomes nearly constant at a value
about $7·5 \times 10^{-3}$ gram-molecules per litre. This is probably almost
entirely non-ionised. The following experiments show that mag-
nesium carbonate is only slightly ionised, even at high dilutions.

Air was drawn through water containing magnesium carbonate

in suspension at 25°. The percentage of carbonic acid in the air was determined by drawing it through an $N/10$-solution of sodium carbonate and determining the proportion of hydrogen carbonate and carbonate.

Total magnesium in solution $= 15\cdot96 \times 10^{-3}$ gram-equivalents per litre. Hydrogen carbonate $= 63\cdot97$ per cent.; carbonate $= 36\cdot03$ per cent. Concentration of free carbonic acid $= 0\cdot0103 \times 10^{-3}$:

$$k_c = \frac{10\cdot21^2}{2\cdot87 \times 0\cdot0103} = 3520.$$

A similar experiment was made with a solution of about the same concentration, but no solid was present.

Total magnesium in solution $= 18\cdot65 \times 10^{-3}$ gram-equivalents. Hydrogen carbonate $= 60\cdot48$ per cent.; carbonate $= 39\cdot52$ per cent.:

$$k_c = \frac{11\cdot28^2}{3\cdot42 \times 0\cdot0103} = 3612.$$

The mean value of k_c is 3566 for a concentration of $17\cdot3 \times 10^{-3}$ equivalents. Taking the ionisation of the magnesium hydrogen carbonate as equal to that of magnesium nitrate, say, $0\cdot84$, we calculate β as follows:

$$\beta = \frac{3566}{7124}\, a^2 = 0\cdot353.$$

Evidently even at an equivalent concentration of $17\cdot3 \times 10^{-3}$ magnesium carbonate is only slightly ionised. From the above experiments we calculate the relation:

$$\frac{[\mathrm{Mg}] \times [\mathrm{CO_3}]}{[\mathrm{MgCO_3}]} = 5\cdot5 \times 10^{-3}.$$

It would be possible by careful experiments to determine β for higher concentrations, but it is evident that at such concentrations as obtained in Engel's experiments the magnesium carbonate will be practically non-ionised. Some experiments of Treadwell and Reuter (*Zeitsch. anorg. Chem.*, 1898, **17**, 200) are unfortunately not available for calculating β, since the solutions are not in true equilibrium with the gaseous phase, but they show that beyond concentrations of magnesium of 50×10^{-3} equivalents the amount of carbonate is practically constant. The maximum value is $9\cdot0 \times 10^{-3}$ gram-molecules per litre. We will take this as the concentration of the non-ionised carbonate in Engel's experiments. These were carried out at $12\cdot5°$. The concentration of the free carbonic acid has to be calculated from the pressure, which is not strictly correct for carbonic acid:

Pressure. Atmospheres.	$C_{Mg}-9$.	α.	[Mg].	[HCO$_3$].	[H$_2$CO$_3$].	$\frac{k_2}{k_3}k_1$.
0·5	245×10^{-3}	0·686	$168\cdot1 \times 10^{-3}$	$336\cdot2 \times 10^{-3}$	$21\cdot55 \times 10^{-3}$	88·17
1·0	316	0·680	219·8	429·6	41·80	94·80
1·5	374	0·675	252·4	504·8	60·9	105·6
2·0	407	0·672	273·5	547·0	79·8	102·5
2·5	435	0·670	291·5	583·0	99·75	99·3
3·0	456	0·669	305·0	610·0	116·4	97·5
4·0	509	0·666	339·0	678·0	151·6	102·8
6·0	603	0·662	399·2	798·4	217·2	117·2

Mean............... 100·57

The concentration of the CO$_3$ ion is calculated from the relation:

$$[CO_3] = \frac{[HCO_3]^2}{[H_2CO_3] \times 7120}.$$

From these figures we may calculate the value of the "solubility product," $[Mg] \times [CO_3]$, namely, $141\cdot2 \times 10^{-6}$.

These estimates of the "solubility product" must be subject to correction for the value of $\frac{k_2}{k_3}$ which is strictly only known for 25°.

Conclusions.

(1) Lithium carbonate is ionised to the same extent as sodium carbonate. The ionisation takes place in two stages, $Li_2CO_3 = Li + LiCO_3$ and $LiCO_3 = Li + CO_3$. Consequently, the concentration of the lithium ion is more than double that of the CO$_3$ ion, and can be calculated. If this is done, it is found that the "solubility product," $[Li]^2 \times [CO_3]$, is practically constant over a wide range, thus confirming the assumption made.

(2) The solubility product of calcium carbonate, $[Ca] \times [CO_3]$, is about $71\cdot9 \times 10^{-10}$, and has hitherto been put at too high a value. It is shown that this agrees with a solubility of calcium carbonate in pure water of $[Ca] = 14\cdot6 \times 10^{-5}$, and that the salt is hydrolysed to the extent of 66 per cent.

(3) Crystallised magnesium carbonate has no definite solubility in pure water. It decomposes into basic carbonates and magnesium hydrogen carbonate, whilst a certain amount of carbonate is also dissolved. Over a wide range, the reaction approximates to $5MgCO_3 + 2H_2O = 3MgCO_3,Mg(OH)_2 + Mg(HCO_3)_2$. The larger the amount of carbonate in relation to the water the larger is the amount of dissolved hydrogen carbonate, but the carbonate tends to reach a limit.

(4) It is shown that at an equivalent concentration of $17\cdot3 \times 10^{-3}$ magnesium carbonate is only ionised (as regards the CO$_3$ ion) to the

extent of about 35 per cent., and probably at high concentrations it is only very slightly ionised.

The "solubility product" of magnesium carbonate at concentrations of free carbonic acid at which the carbonate is a stable solid phase has been calculated from Engel's experiments, and is found to have the value 141×10^{-6}.

[*Received, August 25th*, 1917.]

International Atomic Weights.

THE Council has ordered the following letter and Table to be printed in the Journal of the Society:

WHINFIELD,
SALCOMBE,
S. DEVON.
October 1st, 1917.

DEAR SIRS,

I beg to inform you that the International Atomic Weight Committee have decided to intermit their Annual Reports, owing primarily to the fact that certain of its members are largely occupied with matters arising out of the War, and that it has been found difficult owing to the interruption of communications to keep in correspondence. Furthermore—and this is the more important circumstance—practically all experimental work on the subject of Atomic Weights is for the time being interrupted; indeed, with the entrance of the United States of America into the War, it may be said to be for the present wholly at an end, and no memoir of importance has made its appearance since the issue of the last Report.

As no change has been shown to be required in the Table last published, it is suggested that it should be reprinted as it stands and regarded as current for 1918.

I am, GENTLEMEN,
Your obedient Servant,
T. E. THORPE.

The Hon. Secretaries,
    The Chemical Society,
        Burlington House,
            London, W.

1918.

International Atomic Weights.

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·88	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·68
Barium	Ba	137·37	Niton (radium emanation)	Nt	222·4
Bismuth	Bi	208·0	Nitrogen	N	14·01
Boron	B	11·0	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·00
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·005	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·9
Chlorine	Cl	35·46	Radium	Ra	226·0
Chromium	Cr	52·0	Rhodium	Rh	102·9
Cobalt	Co	58·97	Rubidium	Rb	85·45
Columbium	Cb	93·1	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	44·1
Erbium	Er	167·7	Selenium	Se	79·2
Europium	Eu	152·0	Silicon	Si	28·3
Fluorine	F	19·0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	Ga	69·9	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·06
Glucinum	Gl	9·1	Tantalum	Ta	181·5
Gold	Au	197·2	Tellurium	Te	127·5
Helium	He	4·00	Terbium	Tb	159·2
Holmium	Ho	163·5	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·4
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	118·7
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·84	Tungsten	W	184·0
Krypton	Kr	82·92	Uranium	U	238·2
Lanthanum	La	139·0	Vanadium	V	51·0
Lead	Pb	207·20	Xenon	Xe	130·2
Lithium	Li	6·94	Ytterbium (Neoytterbium)	Yb	173·5
Lutecium	Lu	175·0	Yttrium	Yt	88·7
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·6			

LXXXVI.—*The Temperature of Ignition of Gaseous Mixtures.*

By JAMES WALLACE McDAVID.

NUMEROUS methods for the determination of the ignition-temperature of gaseous mixtures are to be found in the literature, and these have already been classed into three groups by Dixon and Coward (T., 1909, **95**, 514) in their paper on this subject.

The experimental conditions governing this division are as follows:

I. A bulb containing the gaseous mixture was plunged into a bath which was maintained at a constant temperature.

II. A mixture of the gases was passed through a tube in a bath which was gradually being heated.

III. The gaseous mixture was compressed adiabatically, and from the pressure required to ignite it, the temperature of the mixture at the ignition-point was calculated.

In each of the above methods, the gaseous mixture is retained in the state necessary for ignition for some considerable time, and it is quite possible, therefore, that before the ignition-temperature is reached a state of slow combustion ensues which generates sufficient heat to raise the remainder of the gaseous mixture to its ignition-point.

With regard to the third method, which was that used by Falk (*J. Amer. Chem. Soc.*, 1906, **28**, 1517; 1907, **29**, 1536), Dixon and Coward point out that the temperature of ignition of a gaseous mixture under abnormal pressure may be totally different from that of the same mixture under normal pressure.

In the method adopted by Dixon and Coward, the two gases were allowed to flow through two concentric tubes, which were heated in an electric furnace, and allowed to mix at the top of the shorter (inner) tube. A thermo-couple was placed near to the nozzle of the inner tube. In these experiments, in addition to the time factor, the fact that the gases are flowing must also be taken into consideration, and the results obtained by these authors show that the rate of flow and the size of the nozzle of the inner tube affect the results; for example, when the rate of flow of hydrogen was very slow, namely, 2·4 c.c. per minute, and the rate of flow of oxygen was 50 c.c. per minute, the temperature of ignition was 792°, whilst when the rate of flow of hydrogen was 19 c.c. per minute, oxygen still flowing at 50 c.c. per minute, the ignition-temperature was found to be 599°. These authors,

however, give in their paper a definition as to what they have taken as the temperature of ignition

It seems that it is advisable to eliminate as far as possible the time factor in determining the ignition-temperature, and it is also preferable to have a stationary volume of gas.

In table I the results obtained by various workers for several gaseous mixtures are given.

TABLE I.

Ignition-temperatures of Different Gaseous Mixtures.

Gases.		Observer.	Reference.	Temperature of ignition found.
Hydrogen and Oxygen.		Meyer, Krause, Askenasy.	*Annalen*, 1891, **264**, 85 ; *ibid.*, 1892, **269**, 49, 2421 *Zeitsch. physikal. Chem.*, 1893, **11**, 28.	518—606°
,,	,,	Bodenstein.	*Ibid.*, 1899, **29**, 665.	653—710
,,	,,	Meyer and Freyer	*Ber.*, 1892, **52**, 662	700
,,	,,	Gautier and Hélier	*Compt. rend.*, 1896, **122**, 556	840
,,	,,	Hélier	*Ann. Chim. Phys.*, 1897, [vii], **10**, 521.	845
,,	,,	Falk	*J. Amer. Chem.Soc.*, 1906, **28**, 1517 ; 1907, **29**, 1536.	514—540
,,	,,	Dixon and Coward	T., 1909, **95**, 514	580—590
Methane and Oxygen.		Meyer and Freyer	*Zeitsch. physikal. Chem.*, 1893, **11**, 28.	606—650
,,	,,	Meyer and Munch	*Ber.*, 1893, **26**, 2421	656—678
,,	,,	Dixon and Coward	*loc. cit.*	556—700
Ethylene and Oxygen.		Meyer and Freyer	,,	530—606
,,	,,	Meyer and Munch	,,	577—590
,,	,,	Dixon and Coward	,,	500—519
Carbon monoxide and oxygen		Meyer and Freyer	,,	650—730
,,	,,	Meyer and Munch	,,	Combined quietly
,,	,,	Dixon and Coward	,,	637, 658

The methods now described eliminate, so far as is practically possible, the time factor. The temperature of ignition in these experiments is taken to be that temperature to which the gaseous mixture must be heated by the application of a hot body, so as to cause instantaneous ignition.

The temperature of ignition has in the present work only been determined for various gases when mixed with air. Dixon and Coward have, however, shown that there is very little difference in the temperature found when air or oxygen respectively is employed.

The first set of experiments described below was originally undertaken with a view to obtain comparative values for the temperatures of ignition of various gases, but the results seemed of sufficient value to warrant further work being carried out. As a consequence, numerous variations and improvements were introduced, and finally a method was devised which was simple, rapid, and capable of giving accurate results

Details of all the variations of the method have, however, been included, as several of them appear to be useful for comparative purposes at least, although not sufficiently accurate for the determination of absolute values. The results obtained by the method finally adopted for the ignition-temperatures of the various gases tested are given below:

Coal gas–air	878°
Ethylene–air	1000
Hydrogen–air	747
Carbon monoxide–air	931
Petrol (fraction 0—80°)–air	995
Benzene–air	1062
Ether–air	1033

EXPERIMENTAL.

The essence of the method employed in the following experiments consists in the ignition of a small volume of the gaseous mixture contained in a soap bubble by means of an electrically heated wire or other red-hot body, the temperature at which ignition just takes place being noted.

A quantity of the gas to be experimented on was mixed with air and made up to the required concentration in a 10-litre gas holder. To the outlet tube of the holder was attached a piece of capillary tubing terminating in a bulb tube, shaped like the head of an ordinary tobacco pipe. This tube when not in use dipped into a solution of sodium oleate and glycerol in water.

The apparatus employed for igniting the gas consisted of a platinum wire measuring about 0·025 cm. in diameter, which was wound evenly round a small thin-walled silica tube. A thermocouple made of platinum–rhodium which had previously been carefully standardised against a standard pyrometer was passed through the inside of the silica tube so that the thermo-junction was in the centre of the tube. The terminals of the thermocouple were connected to a millivoltmeter, from which the temperature could be read off. The experiments were carried out in a darkened room, as in some cases the flame of the ignited gas was almost invisible in daylight.

The procedure was as follows: When all the connexions had been made, the heating current, which could be varied by means

R R 2

of a rheostat, was switched on. When the temperature as indicated by the millivoltmeter was constant, the tap of the gas holder was opened, and the mixture, flowing through the pipe stem and soap solution, produced a bubble. The tap was closed and the bubble still on the end of the pipe was placed in contact with the hot coil. Ignition was instantaneous, and was usually accompanied by a slight explosion, but in some cases this was so faint as to be detected only with difficulty. The temperature was varied over 60—80° until a sufficient number of readings had been obtained.

The gases employed in the first instance were prepared as follows:

Hydrogen.—From pure zinc and sulphuric acid.

Methane.—By the action of a zinc–copper couple on methyl iodide. The gas was passed through a tube containing more of the zinc–copper couple in order to free it from methyl iodide vapour.

Ethylene.—By passing alcohol vapour over heated aluminium oxide. The gas obtained contained 9 per cent. of methane.

Coal Gas.—Samples were taken from time to time from the local gas supply.

Petrol.—Commercial petrol was fractionated, and 2 c.c. of the fraction boiling between 0° and 80° were vaporised and made up to 10 litres with air.

Benzene and Ether.—Pure chemicals were used, and vaporised as in the case of petrol.

The results found are given in the following tables.

TABLE II.

Comparison of Coal Gas–Air and Methane–Air Mixtures:
90·5 per cent. of Air in Mixture.

Rotherham gas.		Ardeer coal gas.		Methane.	
Temperature.	Result.	Temperature.	Result.	Temperature.	Result.
760°	No ignition	760°	No ignition	840°	No ignition
760	,,	780	Ignition	860	,,
765	,,	780	No ignition	865	,,
780	,,	780	,,	870	,,
790	,,	790	,,	880	,,
790	,,	790	,,	880	,,
795	,,	795	Ignition	880	,,
800	Ignition	795	,,	880	,,
805	,,	800	No ignition	880	,,
805	,,	800	Ignition	880	Ignition
810	,,	800	,,	880	,,
810	,,	800	,,	880	,,
830	,,	810	,,	890	,,
840	,,	820	,,	920	,,

Temp. of ignition = 800°. Temp. of ignition = 800°. Temp. of ignition = 880°.

TABLE III.

Comparison of Coal Gas, Methane, and Hydrogen–Air Mixtures: 86·5 per cent. of Air Present.

Rotherham coal gas.		Ardeer coal gas.		Hydrogen.		Methane.	
Temperature.	Result.	Temperature.	Result.	Temperature.	Result.	Temperature.	Result.
780°	No ignition	800°	No ignition	670°	No ignition	860°	No ignition
785	,,	800	,,	680	,,	870	,,
785	,,	805	,,	680	,,	875	,,
800	,,	805	,,	690	,,	875	Ignition
800	,,	805	Ignition	690	,,	880	No ignition
800	Ignition	810	No ignition	690	,,	885	Ignition
800	,,	810	,,	690	Ignition	885	,,
805	No ignition	810	,,	690	,,	890	,,
815	Ignition	810	Ignition	700	No ignition	900	,,
815	,,	810	,,	700	Ignition	910	,,
		815	,,	700	,,		
		820	,,	710	No ignition		
		820	,,	710	Ignition		
				710	,,		
				720	,,		
Temp. of ignition = 805°.		Temp. of ignition = 810°.		Temp. of ignition = 695°.		Temp. of ignition = 885°.	

TABLE IV.

Comparison of Petrol and Ethylene–Air Mixtures.

Mixture of 9·1% C_2H_4, 0·9% CH_4, and 90% air.			Mixture of 2·0 c.c. petrol (0—80°) vaporised and made up with air to 10 litres.		
Temperature.	No. of readings.	Result.	Temperature.	No. of readings.	Result.
845°	1	Ignition	900°	3	Ignition
840	2	,,	890	3	,,
830	7	,,	880	6	,,
825	8	,,	880	7	No ignition
825	1	No ignition	875	2	Ignition
820	4	Ignition	875	5	No ignition
820	12	No ignition	870	5	,,
815	3	,,	865	2	,,
810	3	,,			
Temp. of ignition = 825°.			Temp. of ignition = 885°.		

A second series of experiments was carried out in which the heating coil was replaced by a semi-cylindrical piece of iron, about 3·75 cm. long by 1·9 cm. in diameter, covered round the circumference with thick asbestos cloth (No. 1 iron block). Running down the centre of the flat surface and about 0·08 cm. under the surface was a small hole to carry the thermo-couple. The block was hung by two platinum wires from a stand. It was then heated until about 50° above the required temperature, when the

blowpipe was removed and bubbles of gas were brought into contact with the red-hot surface while the latter was cooling. When the temperature became too low for ignition to take place, the block was simply heated again and the procedure carried out as before until a sufficient number of readings had been obtained.

An improvement was made in No. 2 block by boring a small hole in the centre of the flat face. By this means, the thermocouple became exposed to the air, and since it lay close to the surface it ought to give a comparatively true figure for the temperature of the igniting surface. Tables V—VIII give comparative results found by the above three methods.

TABLE V.

Comparison of Iron Block and Electric Coil Method with 13·5 per cent. Coal Gas–Air Mixture.

Electric coil method.			Iron block (No. 1 Block) method.		
Temperature.	No. of readings.	Result.	Temperature.	No. of readings.	Result.
770°	3	No ignition	720°	1	No ignition
775	2	,,	730	2	,,
780	4	,,	740	3	,,
780	2	Ignition	750	2	,,
785	1	No ignition	760	1	Ignition
785	1	Ignition	765	1	,,
790	1	No ignition	770	1	,,
790	3	Ignition	790	2	,,
795	1	,,	800	2	,,
800	1	,,	810	1	,,
810	1	,,			

Temp. of ignition = 785°.   Temp. of ignition = 760°.

TABLE VI.

Comparison of Electric Coil and Iron Block Method: 15 per cent. of Hydrogen with Air.

Electric coil.			No. 1 iron block.			No. 2 iron block.		
Temperature.	No. of readings.	Result.	Temperature.	No. of readings.	Result.	Temperature.	No. of readings.	Result.
690°	2	Ignition	720°	6	Ignition	705°	2	Ignition
685	2	,,	710	9	,,	700	4	,,
680	3	,,	705	3	,,	695	3	,,
675	2	,,	705	3	No ignition	690	4	,,
675	3	No ignition	700	7	,,	685	3	,,
670	4	,,	695	3	,,	680	2	,,
665	1	,,	690	3	,,	680	6	No ignition
660	1	,,				675	2	,,
						670	6	,,
						665	1	,,

Temp. of ignition = 680°.   Temp. of ignition = 705°.   Temp. of ignition = 685.

TABLE VII.

Mixture of Two Volumes of Hydrogen with Five Volumes of Air: Two Series Carried Out with No. 2 Iron Block.

Temperature.	No. of readings.	Result.	Temperature.	No. of readings.	Result.
730°	3	Ignition	730°	2	Ignition
720	3	,,	725	1	,,
715	1	,,	720	3	,,
710	2	,,	715	1	,,
705	1	,,	710	5	,,
700	1	,,	700	2	,,
700	1	No ignition	695	3	No ignition
695	3	,,	690	4	,,
690	1	,,	685	1	,,
685	1	,,	680	2	,,
680	1	,,	670	1	,,

Temp. of ignition = 700°.   Temp. of ignition = 700°.

TABLE VIII.

Comparison of Electric Coil and Iron Block Methods: 13·5 per cent. Mixture of Coal Gas with Air.

Electric coil.			No. 1 iron block.			No. 2 iron block.		
Temperature.	No. of readings.	Result.	Temperature.	No. of readings.	Result.	Temperature.	No. of readings.	Result.
785°	6	Ignition	810°	6	Ignition	800°	3	Ignition
782	3	,,	805	1	,,	795	1	,,
780	3	,,	800	1	,,	790	3	,,
775	3	,,	795	3	,,	785	2	,,
775	1	No ignition	795	2	No ignition	780	2	,,
772	2	Ignition	790	1	Ignition	775	2	,,
772	5	No ignition	790	3	No ignition	770	3	,,
770	3	,,	785	1	,,	770	1	No ignition
768	3	,,	780	4	,,	765	3	Ignition
765	1	Ignition	775	3	,,	765	3	No ignition
765	3	No ignition				760	3	,,
760	1	,,				755	1	,,
						750	2	,,

Temp. of ignition = 775°.   Temp. of ignition = 795°.   Temp. of ignition = 765°.

From the results given in tables II—VIII, it will be observed that the method gives a very sharp ignition-point, and since the time taken to determine the temperature of ignition of any mixture was only about fifteen minutes, it is evident that for purposes of comparison at least the method is very suitable.

It will also be noted from the above results that the concentration of the explosive gas has, within the explosion limits, no effect on the temperature of ignition.

As, however, the rate of cooling in the iron block method was

very rapid, the method was not very satisfactory for the purpose of obtaining absolute values. Accordingly, it was discarded in favour of the method first described. Even in this method there are several factors that may affect the absolute value of the results whilst in no way affecting their comparative value. These factors are the cooling effect of the bubble, the presence of moisture in the gases, the catalytic action of the platinum wire, and the size of the silica tube.

Dixon and Coward (*loc. cit.*) showed that the presence of moisture did not affect the ignition-temperature in the case of hydrogen and oxygen, and in several other cases the difference was very small.

The cooling effect of the bubble need not be taken into account, as its mass was very small compared with that of the heating source. Moreover, although it was found that variations in the size of the bubble gave small differences in temperature, this was probably due to a different cause, which is explained later.

The chief defect in this method lay in the fact that the temperature registered by the thermo-couple was probably slightly lower than that of the coil, since the former was separated from the coil by the thickness of the silica and a volume of air. It is, of course, obvious that the thermo-junction ought to be near to the centre of the tube and that the coil must be as evenly wound as possible, so that there may be no unequal heating.

In order to study the effect of the size of the silica tube on the temperature recorded by the thermo-couple, and, if possible, to obtain absolute values for the temperature of ignition of various gases, a large number of determinations was carried out. For this purpose, the gases employed were obtained in as pure a state as possible, and on analysis gave the following results:

Per cent.

Hydrogen .... $\begin{cases} H_2 & = 99\cdot6 \\ CO_2 & = 0\cdot4 \end{cases}$

Carbon monoxide .... $\begin{cases} CO & = 94\cdot0 \\ Air & = 6\cdot0 \end{cases}$

Ethylene .... $\begin{cases} C_2H_4 & = 93\cdot8 \\ Air & = 6\cdot2 \end{cases}$

Methane (natural gas) .... $\begin{cases} CH_4 & = 95\cdot36 \\ CO & = 0\cdot50 \\ C_2H_4 & = 0\cdot31 \\ H_2 & = 1\cdot43 \\ N_2 & = 2\cdot40 \end{cases}$

In making up the gaseous mixtures, allowance was always made for the quantity of air present in the gas.

Table IX gives the dimensions of the various silica tubes employed in the determinations. These were drawn out as evenly as possible from ordinary silica tubing.

The experiments were carried out in the same manner as before, except that the ends of the silica tubes were in all cases stopped up with asbestos fibre so as to diminish loss of heat within the tube by convection. Platinum and Eureka resistance wire were employed for making the ignition coils. The results found for hydrogen are given in table IX.

TABLE IX.

Showing Effect of the Size of the Silica Tube on the Temperature of Ignition of Hydrogen.

No. of tube.	Thickness of wall of tube. (cm.)	Internal diameter. (cm.)	Length. (cm.)	Temperature of ignition of 20 per cent. of hydrogen in air using	
				Eureka wire.	Platinum wire.
1	0·055	0·1575	6	682°	712°
2	0·035	0·1475	6	688	712
3	0·030	0·12	6	{ 690 / 695 }	—
4	0·0425	0·0775	6	{ 710 / 712 / 712 }	—
5	0·030	0·075	3	735	—
6	0·035	0·075	6	726	{ 735 / 735 }
7	0·035	0·095	5·5	—	725
8	0·0275	0·0775	6·0	735	—
9	0·0225	0·065	4·0	735	758
10	0·025	0·065	4·0	735	—

It will be observed, in the first place, that for the same tube the figures found by using platinum are higher than those obtained when using Eureka wire, indicating a catalysing effect in the case of the latter. It is, however, probable that both substances exert a catalytic influence.

It will also be noticed that as the thickness of the wall and the internal diameter of the silica tube decreased, the temperature of ignition increased.

It was not found possible to make tubes of smaller size than No. 9, and it was therefore impossible to say whether or not the temperature given by No. 9 were a maximum. It seemed probable, however, that the temperatures found when using this tube were very near to the actual temperature of the heating coil.

Accordingly, this tube wound with platinum wire was used to

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determine the temperatures of ignition of other gases, and the results found are summarised below:

Hydrogen–air .... 758°
Carbon monoxide–air 910
Ethylene–air .... 895—905
Coal gas–air 850
Petrol–air 960
Methane–air .... No ignition below 1000°.

In tables I and II the ignition-temperature of methane in air was found to be 880—885°, but the gas probably contained a considerable quantity of hydrogen. In order to verify this supposition, the effect of adding different proportions of hydrogen to methane–air mixtures was studied, with the following results:

TABLE X.

Showing Effect of Hydrogen on the Temperature of Ignition of Methane and Air.

Gaseous mixture.	Temperature of ignition.
1000 c.c. methane 1000 ,, hydrogen 8000 ,, air }	.... 796°
1500 c.c. methane 500 ,, hydrogen 8000 ,, air }	.... 835°
1850 c.c. methane 150 ,, hydrogen 8000 ,, air }	.... No ignition up to 970°.

It is thus evident that pure methane when mixed with air does not ignite below 1000°. This fact is interesting, and receives some confirmation from a statement in Brunswig's "Explosives" (English edition, p. 55), in which it is stated that in the case of methane and air there is delayed ignition at 600° to 700°, but that instantaneous ignition does not take place below 1000°.

The foregoing experiments, although interesting, were, however, not quite conclusive, but it was hoped that by making use of an instrument called the meldometer, invented by Professor Joly, corroboration of the above results would be obtained.

This instrument consists essentially of an apparatus for measuring accurately the expansion of a platinum strip when subjected to heat. The strip, which is held between two arms, one fixed and the other movable, is heated electrically, and thus expands. Since the linear expansion in the case of platinum is almost directly proportional to the temperature, it is sufficient to note the length of the strip at one or two fixed temperatures in order

to find out by interpolation the temperature corresponding with any given length of the strip.

Unfortunately, the experiments carried out with this apparatus were unsuccessful. The strip was so very thin that when a bubble of the gaseous mixture was brought in contact with it, slow combustion first ensued which raised the temperature of the strip until the latter glowed, and thus exploded the residue of the gas. The method of standardising this instrument, however, indicated a method of standardising the apparatus used in the first series of experiments described herein. The apparatus finally employed, the method of standardisation, and the results obtained are described below.

The ignition apparatus in this final series of experiments consisted of a platinum coil wound regularly round two mica strips 3 cm. in length by about 0·3 cm. in width. These strips were notched along the edges so as to hold the wires in position, whilst between them, and thus insulated from the heating coil, was placed a platinum–platinum–rhodium thermo-couple. The wire used for the heating coil was about 0·025 cm. in diameter, and the pitch of the spiral was equal to about the diameter of the wire. The heating current was provided by storage batteries in order to obtain no fluctuations in the temperature, and the latter was varied by means of a sliding resistance.

An ammeter was also placed in the circuit in order to measure the current.

The thermo-couple, which had previously been standardised against a standard thermo-couple, was connected to a millivoltmeter. It will be noticed later, however, that it was unnecessary to use a standardised thermo-couple; in fact, it was ultimately found that no thermo-couple was necessary, as the required results could be obtained by simply reading the ammeter. The apparatus was standardised in the following manner.

Four salts the melting points of which were accurately known were selected and purified. A few crystals of each were ground to a powder, and a small quantity of this powder was deposited on the platinum spiral. The current was then turned on and the coil heated, the temperature being slowly raised until the salt just melted. A rough experiment was carried out first in each case to find out the approximate melting point, the determination being then repeated several times with great care.

It was found when the melting points of the salts were taken from time to time during the experiments that the readings on the millivoltmeter varied considerably, but that the ammeter readings were practically constant for the same temperature.

The variation in the millivoltmeter readings may have been due to various causes, for example, the alteration in zero point of the instrument, variation in room temperature, or to the thermo-couple having been accidentally moved from the centre of the coil during the experiments. The ammeter readings, therefore,
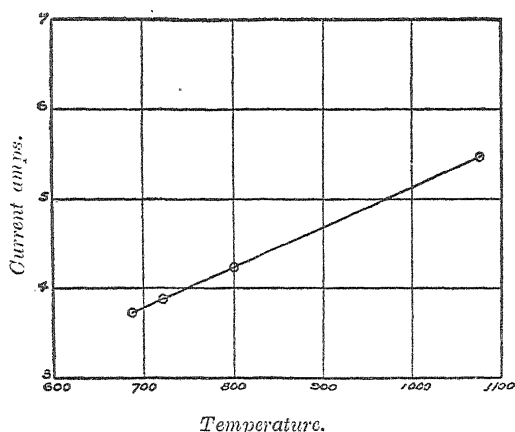
Temperature.

Curve connecting ammeter readings with actual temperature.
Standardised 1.5.16 and 2.5.16.

only have been recorded. Table XI gives the results obtained on standardising the apparatus before and after use.

TABLE XI.

| | | Ammeter readings. | |
Salt employed.	True m.p.	Before experiments.	Before experiments.
Potassium iodide	687°	3·74	3·76
Potassium bromide ...	723	3·90	3·90
Sodium chloride	800	4·22	4·22
Potassium sulphate ...	1072	5·45	5·47

The curve connecting the ammeter readings with the true temperature is shown in the figure.

Table XII gives the analysis of the gases employed.

TABLE XII.

Analysis of Gases Used.

			Coal gas.	Ethylene.	Hydrogen.	Carbon monoxide.
CO_2	per cent.	......	0·26	—	—	—
O_2	,,	......	0·47	—	—	—
C_2H_4	,,	......	4·53	94·0	—	—
CO	,,	......	9·84	—	—	97·5
CH_4	,,	......	50·30	—	—	—
H_2	,,	......	33·00	—	95·8	—
N_2	,,	......	1·60	—	—	—
Air	,,	......	—	6·0	4·2	2·5

In table XIII, the results found for the temperature of ignition of various mixtures of gases with air are given. In cases where the gas contained air as impurity, this was allowed for in making up the mixture.

TABLE XIII.

Ignition-temperatures of Different Inflammable Gas–Air Mixtures.

Mixture.	Ammeter reading.	True temperature of ignition.
15% coal gas–air	4·59	878°
10% ethylene–air	5·12	1000
10% hydrogen–air	4·00	747
Carbon monoxide–air	4·82	931
Petrol (b.p. 0—80°)–air	5·10	995
Benzene–air	5·41	1062
Ether–air	5·27	1033

It was found that by enlarging the size of the bubble, the mixture could be made to ignite at an apparently lower temperature. This, however, was probably due to the fact that slow combustion of part of the gas took place at the lower temperature, and, by heating the surrounding gas, caused it to ignite without showing a corresponding rise on the ammeter. This ignition was, as a rule, quite perceptibly delayed. By reducing the size of the bubble to about 3·7 cm. diameter, instantaneous ignition occurred. The results given in table XIII are the mean of a large number of experiments, and experimental error can be taken as being less than ±3°.

LXXXVII.—*Disodium Nitrite, an Additive Compound of Sodium Nitrite and Sodium.*

By Edward Bradford Maxted.

In the course of work on the preparation of alkali metals by the electrolysis of non-aqueous solutions, the author had occasion to examine the products obtained by electrolysing a solution of sodium nitrite in perfectly anhydrous liquid ammonia. A deposit was observed to form on the cathode, resembling metallic sodium in that it dissolved in water with violent evolution of hydrogen, but completely differing from the metal by reason of its bright yellow colour and by its failure to dissolve in excess of ammonia with the production of the characteristic blue coloration.

It was found, further, that the same compound may be obtained in a state of purity, as a brilliant yellow precipitate, by bringing together free metallic sodium and dry sodium nitrite, each dissolved separately in anhydrous ammonia. An analysis of the precipitate showed it to possess the empirical composition Na_2NO_2, the ammonia acting merely as a solvent. By the action of water, decomposition takes place with regeneration of sodium nitrite and of sodium hydroxide. No hyponitrite could be detected in the solution.

Experimental.

Direct Preparation of Disodium Nitrite.

For the preparation of the compound in a pure condition, it is essential first of all to free the ammonia, which is to be used as a solvent, from all traces of moisture. This may be done by introducing into a distilling flask a suitable quantity of liquid ammonia and dissolving in it sufficient sodium to impart to it a blue colour. The ammonia is freed from sodium hydroxide and from excess of sodium by distillation and recondensation in the vessel which is to be used for the preparation of disodium nitrite.

The preparation may most conveniently be carried out by dissolving in the clear, anhydrous ammonia thus obtained a known weight of metallic sodium, this being added in small pieces. Freshly fused and finely powdered sodium nitrite in a solid condition is next introduced. It is found unnecessary to dissolve this separately provided that sufficient time is given for the sodium to pass into solution and that '' 'trite is added gradually. The addition of sodium to a solution of sodium nitrite, on the other

hand, does not result in a satisfactory preparation on account of the formation of an insoluble layer round the sodium as added.

The completion of the reaction is easily recognised by the discharge of the deep blue colour. This is found to take place on the addition of one molecule of sodium nitrite to each atom of sodium, disodium nitrite being thrown down as a bright yellow precipitate, from which the excess of ammonia is removed by evaporation. Any access of moisture is accompanied by an explosion, which is usually sufficiently intense to shatter the reaction vessel and to cause a dangerous spray of liquid ammonia.

In an experiment, about 100 c.c. of pure anhydrous ammonia were condensed in the long-necked flask used as a reaction vessel. At this stage, the rubber stopper at its mouth was withdrawn and replaced by a second one fitted with a Bunsen valve. One gram of metallic sodium was now introduced gradually in small pieces, the reaction vessel being allowed to remain for about ten minutes after the final addition to ensure complete solution of the sodium. Three grams of finely powdered sodium nitrite, previously dried by fusion, were next weighed out in a small stoppered tube and added gradually to the solution of sodium, the vessel being shaken gently. On adding the last portion of nitrite, the blue coloration in the reaction vessel disappeared, showing that one atom of sodium reacted with each molecule of sodium nitrite, and a yellow precipitate of disodium nitrite was seen to have formed. The reaction vessel was now removed from its cooling-bath and allowed to attain the ordinary temperature, with consequent evaporation of the layer of colourless liquid ammonia with which the compound was covered. At this point, the reaction vessel, together with its stopper and valve, was weighed in order to ascertain whether ammonia was being retained as an integral part of the compound, the following results being obtained:

	Grams.
Weight of empty reaction vessel	52·77
Weight of sodium added	1·00
Weight of sodium nitrite added	3·00
	56·77
Weight of vessel plus compound after evaporation of ammonia	56·79

The yellow compound contains, therefore, no ammonia.

Preparation of Disodium Nitrite by the Electrolysis of Sodium Nitrite.

For this purpose, a reaction tube about 35 cm. long and 3 cm. in internal diameter was provided with concentric cylindrical

platinum electrodes separated from one another by an asbestos diaphragm. The area of the electrode used as cathode was about 25 sq. cm. After half filling the electrolysis tube with pure, dry liquid ammonia in the manner already described, about 5 grams of dry powdered sodium nitrite were introduced and the whole allowed to remain. No metallic sodium was, of course, introduced into the electrolysis vessel.

The two electrodes with their asbestos diaphragm were next introduced into the nitrite solution, care being taken to avoid access of atmospheric moisture, and a current of 2 amperes at a potential of 110 volts from the laboratory mains was led through for one hour. On interrupting the current, the cathode was seen to be covered with and surrounded by a yellow deposit similar to that obtained by the direct action of sodium on the nitrite. The platinum cathode was quickly immersed in a test-tube of dry ether, and on bringing it under water, the vigorous evolution of a considerable quantity of hydrogen was noted. A somewhat striking demonstration of the violence with which the compound combines with water was obtained by repeating the experiment and allowing the yellow cathodic deposit, separated as far as possible from the ammonia, to rise to the ordinary temperature in contact with the air. A series of sharp decrepitations, accompanied often by fire, was observed.

Action of Water on Disodium Nitrite.

In order to examine the moderated action of water on the compound, 4 grams were prepared in a pure, ammonia-free condition by the first method. Hydration was now carried out by the passage of a current of moist nitrogen, distilled water being added as soon as hydration was complete.

The solution was found to exert no reducing action on Fehling's solution, showing the absence of hydroxylamine and similar compounds. A second portion was tested for hyponitrite by neutralising with $N/100$-sulphuric acid, followed by silver sulphate, in accordance with the procedure recommended by Divers and Haga (T., 1899, **75**, 97). No yellow precipitate of silver hyponitrite was obtained. A further sample was now neutralised, without dilution, with $N/10$-nitric acid, and silver nitrate added. A white precipitate soluble in much water was obtained. In order to investigate the composition of this precipitate, which was suspected to be silver nitrite, a further 4 grams of disodium nitrite was hydrated in the manner previously described, made up to approximately 100 c.c., and neutralised as before with $N/10$-nitric

acid. The precipitate obtained by the addition of excess of silver nitrate solution was collected and carefully washed with cold distilled water, after which it was dried in a vacuum desiccator in the dark. A silver salt (2·1 grams) was obtained which was found on analysis to contain $Ag = 69·8$; $AgNO_2$ requires $Ag = 70·1$ per cent.

It is intended, as soon as time permits, to investigate the whole subject more closely, and to examine also the possibility of obtaining alkyl derivatives, which may throw light on the constitution of disodium nitrite.

CHARLES STREET,
WALSALL.   [*Received, September 13th, 1917.*]

LXXXVIII.—*Studies in the Phenylsuccinic Acid Series. Part V. The Inter-conversion of the Esters of* r- *and* meso-*Diphenylsuccinic Acids.*

By HENRY WREN and CHARLES JAMES STILL.

IN the course of the earlier investigations on the optically inactive diphenylsuccinic acids, it was shown by Reimer (*Ber.*, 1881, **14**, 1802) that these substances are mutually transformable. When the *r*-acid is heated with concentrated hydrochloric acid at 200°, the *meso*-acid is quantitatively produced, whilst the converse transformation occurs when *meso*-diphenylsuccinic acid is subjected to the action of an excess of barium hydroxide solution at the same temperature. Somewhat later, Anschütz and Bendix (*Annalen*, 1890, **259**, 91) found that a partial isomerisation takes place when the *r*-acid is heated with water alone at temperatures between 165° and 200°, the *meso*-acid being formed to the extent of approximately 30 per cent. The transition from the *meso*- to the racemic series can be effected, however, under milder experimental conditions when the *meso*-acid is replaced by its ethyl ester as initial material; thus Anschütz and Bendix (*loc. cit.*) showed that potassium *r*-diphenylsuccinate is the sole product of the action of alcoholic potassium hydroxide solution on ethyl *meso*-diphenylsuccinate, whilst, when aqueous alcoholic potassium hydroxide is employed a mixture of potassium *r*- and *meso*-diphenylsuccinates is obtained (Wren and Still, T., 1915, **107**, 447).

The experiments which are now described were undertaken with the hope of more definitely locating the phase at which the change

in stereochemical configuration occurs. This might conceivably take place before, during, or subsequent to the actual hydrolysis. Experiments with the di-*l*-menthyl esters of *meso*- and *l*-diphenylsuccinic acids (Wren and Still, this vol., p. 531) made it appear probable that the change at any rate in part, precedes the hydrolysis, since it was found that the ester of the *l*-acid is converted into that of the *meso*-acid when heated with aqueous alcoholic potassium hydroxide solution; under similar conditions, the ester of the *meso*-acid appeared to suffer isomerisation, but the nature of the product could not be definitely established. As these esters are not readily prepared in considerable quantity and as the di-*l*-menthyl *r*-ester has not yet been obtained, the work has been continued with the more readily accessible methyl and ethyl esters.

When ethyl *r*-diphenylsuccinate is hydrolysed with a deficiency of aqueous ethyl-alcoholic potassium hydroxide solution, the non-hydrolysed portion is found to be composed of a mixture of ethyl *r*- and *meso*-diphenylsuccinates, from which the latter can be readily isolated in the pure state; a similar mixture is formed under like conditions from ethyl *meso*diphenylsuccinate, and from this a pure specimen of the ethyl *r*-ester can be separated, the slightly greater experimental difficulty in this instance being due to the relatively greater solubility of the racemic ester. Precisely similar phenomena are observed with aqueous methyl-alcoholic potassium hydroxide solution and the corresponding methyl esters. The products of the hydrolysis have not been investigated with respect to stereochemical configuration, since they doubtless consist of mixtures of potassium salts of the acids and acid esters, the approximately quantitative separation of which would be a matter of great difficulty.

The experiments just described show that isomerisation, at any rate in part, precedes hydrolysis; it may also take place to some extent subsequently, since potassium *meso*diphenylsuccinate is partly converted into the salt of the *r*-acid when heated with aqueous-alcoholic potassium hydroxide solution. The change in the reverse direction appears to take place far less readily under similar conditions, and could not be definitely proved to occur.

Since it was thus shown that the esters of the *r*- and *meso*-acids are interconvertible under the influence of alkali hydroxides, it appeared of interest to examine their behaviour in the presence of alkaline reagents under conditions which would preclude hydrolysis. For this reason, a series of experiments has been performed with solutions of sodium methoxide and ethoxide in methyl and ethyl alcohols respectively. The conversion of methyl and ethyl *r*-diphenylsuccinates into the corresponding *meso*-esters can thus be

readily effected; the latter are considerably less readily soluble in these solvents than the former, and the conditions can be so chosen that they separate from the solutions. In these circumstances, isomerisation proceeds approximately quantitatively. The reverse change can only be effected in much more dilute solution, and the isolation of the *r*-esters involves a series of fractional crystallisations.

Lastly, the conversion of ethyl *r*- into ethyl *meso*-diphenylsuccinate has been studied under somewhat different conditions. During the last few years it has been frequently necessary to prepare *r*-diphenylsuccinic acid, and the process adopted has been that previously described by us (T., 1915, **107**, 446 *et seq.*), which consists in allowing ethyl phenylacetate and iodine to react in ethereal solution in the presence of solid sodium ethoxide and hydrolysing the mixture of ethyl *r*- and *meso*-diphenylsuccinates which is thus produced. It has been noticed repeatedly that, whilst the yield of *r*-acid is tolerably constant, the proportion of *r*- to *meso*-ester produced in the different experiments varies within very wide limits. The explanation is now found to lie in the observation that ethyl *r*-diphenylsuccinate is converted into the *meso*-ester when its ethereal solution is allowed to remain in contact with solid sodium ethoxide.

From the theoretical point of view, the interconversion of the esters in the presence of alkali appears to be most readily explained by the assumption of the formation of a common sodio-derivative which is decomposed by alcohol according to the scheme:

$$\begin{array}{c} CO_2Et \\ | \\ Ph-C-H \\ | \\ Ph-C-H \\ | \\ CO_2Et \end{array} \quad \underset{EtOH}{\overset{NaOEt}{\rightleftharpoons}} \quad \begin{array}{c} C{<}^{OEt}_{ONa} \\ \| \\ Ph-C \\ | \\ Ph-C-H \\ | \\ CO_2Et \end{array} \quad \underset{EtOH}{\overset{NaOEt}{\rightleftharpoons}} \quad \begin{array}{c} CO_2Et \\ | \\ H-C-Ph \\ | \\ Ph-C-H \\ | \\ CO_2Et \end{array} \quad + \quad \begin{array}{c} CO_2Et \\ | \\ Ph-C-H \\ | \\ H-C-Ph \\ | \\ CO_2Et \end{array}$$
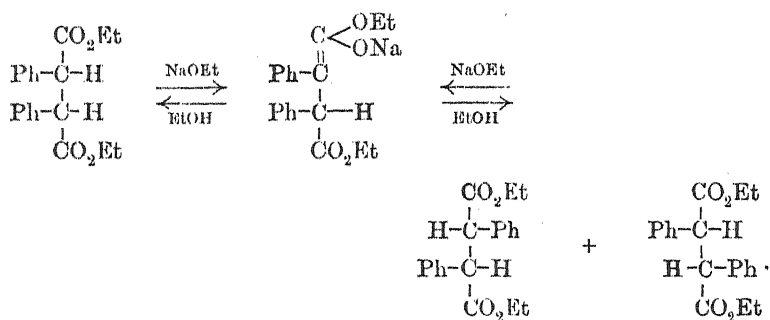
EXPERIMENTAL.

Conversion of Ethyl r-*Diphenylsuccinate into Ethyl* meso*Diphenylsuccinate.*

A. *By Partial Hydrolysis.*—Ethyl *r*-diphenylsuccinate (0·8 gram) was heated under reflux during two and a-half hours with aqueous ethyl-alcoholic potassium hydroxide solution (0·216N, 10 c.c.); the

solution was poured into water and the mixture extracted with ether. The crystalline residue, left after evaporation of the solvent, melted at 76—114°; it was repeatedly crystallised from rectified spirit, whereby needles of ethyl *meso*diphenylsuccinate, melting at 140—141°, were readily isolated.

B. *By the Action of Sodium Ethoxide in Ethyl-alcoholic Solution.* —Ethyl *r*-diphenylsuccinate (1·5 grams) was gently warmed in a small sealed tube with a solution of sodium ethoxide in absolute ethyl alcohol (0·32N, 10 c.c.) until an almost clear solution was formed; on cooling, the contents of the tube set to a stiff paste, which did not change in appearance when preserved for eight days at the temperature of the laboratory. The solid was filtered, washed successively with alcohol, water, dilute hydrochloric acid, water, and alcohol, and dried. It weighed 1·4 grams and melted sharply at 140—141°. The melting point remained unaltered when the substance was crystallised from rectified spirit; it was further identified as ethyl *meso*diphenylsuccinate by the mixed melting-point method and by analysis. (Found, $C = 73·5$; $H = 6·8$. Calc., $C = 73·6$; $H = 6·8$ per cent.)

The filtrate from the original crop was diluted with water, when a small amount of solid was precipitated which melted indefinitely at 78—128°.

C. *By Solid Sodium Ethoxide.*—Finely divided, dry sodium ethoxide (prepared from 1 gram of sodium) was allowed to remain in contact with a solution of ethyl *r*-diphenylsuccinate (1 gram) in anhydrous ether (20 c.c.), at the temperature of the laboratory during twenty-four hours. Water was then added, whereby two clear solutions were formed; the aqueous portion was once extracted with ether and the ethereal solutions were united and dried over calcium chloride. The residue, obtained after removal of the solvent, melted at 75—110°, and, after being twice crystallised from rectified spirit, yielded pure ethyl *meso*diphenylsuccinate. The latter melted at 140—141°, and the melting point remained unchanged when it was mixed with an approximately equal quantity of the synthetic ester.

Conversion of Ethyl meso*Diphenylsuccinate into Ethyl* r-*Diphenylsuccinate.*

A. *By Partial Hydrolysis.*—Ethyl *meso*diphenylsuccinate (5·7 grams) was heated under reflux during two hours with aqueous, ethyl-alcoholic potassium hydroxide solution (0·156N, 60 c.c.). The resulting solution was evaporated nearly to dryness, the residue diluted with water, and shaken with a large volume of chloroform. The extract was dried over calcium chloride and the solvent re-

moved. The residue melted at 76—128°. It was digested with two successive small quantities of boiling light petroleum (b. p. 40—60°). [The part which remained undissolved by this treatment melted at 133—136°, and, after being crystallised from alcohol, yielded unchanged ethyl *meso*diphenylsuccinate, m. p. 140—141°.] The solutions were evaporated to dryness and the united residues extracted with alcohol; the more soluble portion, after being crystallised from light petroleum (b. p. 40—60°), yielded ethyl *r*-diphenylsuccinate. The latter melted at 83·5—84·5°, and the melting point remained unchanged when it was mixed with the synthetic *r*-ester. It was also identified by analysis. (Found, C = 73·4; H = 6·7. Calc., C = 73·6; H = 6·8 per cent.)

B. *By the Action of Sodium Ethoxide in Ethyl-alcoholic Solution.*—Finely divided ethyl *meso*diphenylsuccinate (5 grams) was shaken with a solution of sodium ethoxide in absolute ethyl alcohol (0·32N, 85 c.c.) at 70° during three hours; at the end of this period, the ester had completely dissolved to a pale yellow solution, which was then poured into a slight excess of dilute hydrochloric acid. The mixture was shaken with chloroform and the extract washed with aqueous sodium carbonate solution and dried over calcium chloride. The residue left after evaporation of the solvent melted at 76—128°. The mixture of normal esters, after being treated as described in the preceding paragraph, yielded unchanged ethyl *meso*diphenylsuccinate and ethyl *r*-diphenylsuccinate. The latter melted at 83—84·5°, and no alteration in the melting point was observed when it was mixed with an approximately equal amount of the synthetic *r*-ester.

Conversion of Methyl r-Diphenylsuccinate into Methyl mesoDiphenylsuccinate.

A. *By Partial Hydrolysis.*—Aqueous, methyl-alcoholic potassium hydroxide solution (0·874N, 12 c.c.) was added to a boiling solution of methyl *r*-diphenylsuccinate (3 grams) in methyl alcohol (200 c.c.) and the mixture heated under reflux during four hours. The alcohol was removed by evaporation and the residue treated with water and a large volume of chloroform. The product, obtained after desiccation of the chloroform solution and removal of the solvent, melted at 168—202°. It was twice crystallised from acetone, when methyl *meso*diphenylsuccinate was isolated in well-defined needles which melted at 219—220°. No depression of the melting point was observed after admixture with the synthetic *meso*-ester. The substance was further identified by analysis. (Found: C = 72·6; H = 6·2. Calc., C = 72·5; H = 6·2 per cent.)

B. *By the Action of a Methyl-alcoholic Solution of Sodium*

Methoxide.—Methyl *r*-diphenylsuccinate (1 gram) was suspended in a solution of sodium methoxide in absolute methyl alcohol (0·301N, 50 c.c.) and heated at 50—60° during eleven hours; the ester did not immediately dissolve, but, after about three hours, the nature of the precipitate was observed to have changed, the platelets being replaced by a quantity of very fine needles. After cooling, the precipitate was removed, well washed with water, and crystallised from a considerable bulk of acetone; well-formed, prismatic crystals of methyl *meso*diphenylsuccinate were thus obtained which melted at 218·5—219·5°. The melting point was unchanged when the substance was mixed with the synthetic *meso*-ester.

At the ordinary temperature, the change proceeds very slowly, doubtless owing to the comparatively sparing solubility of the *r*-ester in methyl alcohol. When the ester and alkali solution (approx. 0·25N) were used in the proportion of 1 gram to 20 c.c., no change appeared to have taken place after nine days; after three months, however, the formation of the *meso*-ester could be definitely established.

Conversion of Methyl meso*Diphenylsuccinate into Methyl* r-*Diphenylsuccinate.*

A. *By Partial Hydrolysis.*—Methyl *meso*diphenylsuccinate (3 grams) was partly suspended and partly dissolved in boiling methyl alcohol (380 c.c.); 5 c.c. of aqueous methyl-alcoholic potassium hydroxide solution (0·68N) were added and the mixture was boiled for an hour. A further portion of the alkali solution (5 c.c.) was then added, and the heating was continued for a further period of five hours. At the end of this time, the ester had completely passed into solution. The alcohol was removed and the residue shaken with chloroform and water. The mixture of esters obtained from the chloroform solution melted at 158—196°; it was fractionally crystallised from acetone. Unchanged *meso*-ester was isolated from the less soluble portion, whilst methyl *r*-diphenylsuccinate was obtained by repeated crystallisation of the more soluble part from a considerable bulk of methyl alcohol. The latter was identified by crystalline form, melting point (173—174·5°), mixed melting point, and analysis. (Found: C = 72·3; H = 6·1. Calc.: C = 72·5; H = 6·2 per cent.)

B. *By the Action of a Solution of Sodium Methoxide in Methyl Alcohol.*—Finely divided methyl *meso*diphenylsuccinate (2 grams) was heated in a stoppered flask during ten hours at 60° with a solution of sodium (0·9 gram) in absolute methyl alcohol (200 c.c.). A small portion remained undissolved. The mixture was exactly

neutralised with dilute hydrochloric acid and the alcohol removed on the water-bath. The residue was treated with warm water, and the part which remained undissolved was removed and dried. The mixture of normal esters thus obtained melted indefinitely at 162—182°. It was separated by systematic treatment with acetone and methyl alcohol, as described in the preceding paragraph, into unchanged methyl *meso*diphenylsuccinate and methyl *r*-diphenyl-succinate, the melting points being 218·5—219·5° and 174—175° respectively.

Action of an Excess of Ethyl-alcoholic Potassium Hydroxide Solution on r- *and* meso-*Diphenylsuccinic Acids.*

*meso*Diphenylsuccinic acid (1 gram) was heated under reflux with a solution of potassium hydroxide in absolute ethyl alcohol (0·8*N*, 25 c.c.) during four hours. The substance dissolved slowly, complete solution being ultimately obtained. Excess of alkali was exactly neutralised with hydrochloric acid. The alcohol was removed by evaporation; the residue was dissolved in a small volume of water and treated with a slight excess of a hot solution of barium chloride. On cooling, a crystalline precipitate of barium *r*-diphenylsuccinate separated, from which the corresponding acid was isolated; it melted at 181—182°, resolidified, and again melted at 219—220°. Unchanged *meso*diphenylsuccinic acid, melting and decomposing at 229—230°, was obtained from the filtrate from the crop of barium salt.

r-Diphenylsuccinic acid (1 gram) was heated under reflux with ethyl-alcoholic potassium hydroxide solution (0·8*N*, 25 c.c.). The product was treated exactly as described in the preceding paragraph. Unchanged *r*-acid was readily isolated from the corresponding, sparingly soluble barium salt, the mother liquors from which, however, did not yield *meso*diphenylsuccinic acid in recognisable amount.

LXXXIX.—*Derivatives of* n-*Butylaniline.*

By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

THE lower alkylanilines have for a long period been recognised as of considerable technical importance and, with their derivatives, have been subjected to very detailed investigation. On the other hand, the higher alkylanilines and phenylenealkyldiamines generally have been but little examined, and it is only quite recently that such compounds as p-nitrosodipropylaniline, p-phenylenedipropyldiamine (Jacobs and Heidelberger, *J. Biol. Chem.*, 1915, **21**, 103), and p-phenylene*iso*amyldiamine (Karrer, *Ber.*, 1915, **48**, 1398) have been subjected to any thorough study (compare also Mandl, *Monatsh.*, 1886, **7**, 99; Baeyer and Noyes, *Ber.*, 1889, **22**, 2173). In the case of the n-butyl compounds but few derivatives have been prepared. By condensing n-butyraldehyde with aniline, Kahn (*Ber.*, 1885, **18**, 3361) obtained n-butylaniline, and from it the nitrosoamine, the acetyl compound, and the hydrochloride, but no other references to n-butylaniline or its derivatives have been found.

In the present work the condensation of n-butyl chloride and aniline has been investigated, and several of the derivatives of n-butylaniline have been prepared and their properties investigated. In the reaction between n-butyl chloride and aniline, it was found that mono-n-butylaniline was the chief product when these compounds were heated together under atmospheric pressure. A fraction of higher boiling point was found to consist mainly of di-n-butylaniline.

The crude mixture of bases resulting from the reaction was distilled, and thus partly separated into aniline, n-butylaniline, and di-n-butylaniline. The n-butylaniline fraction was converted into phenyl-n-butylnitrosoamine (I), which was reduced to *as*-phenyl-

$$N(C_4H_9)\cdot NO$$
(I.)

$$N(C_4H_9)\cdot NH_2$$
(II.)

$$N(C_4H_9)\cdot N{:}N\cdot N(C_4H_9)$$
(III.)

$$NH\cdot C_4H_9$$
$$NH_2$$
(V.)

$$NH\cdot C_4H_9$$
$$NO$$
(IV.)

$$N(C_4H_9)\cdot NO$$
$$NO$$
(VI.)
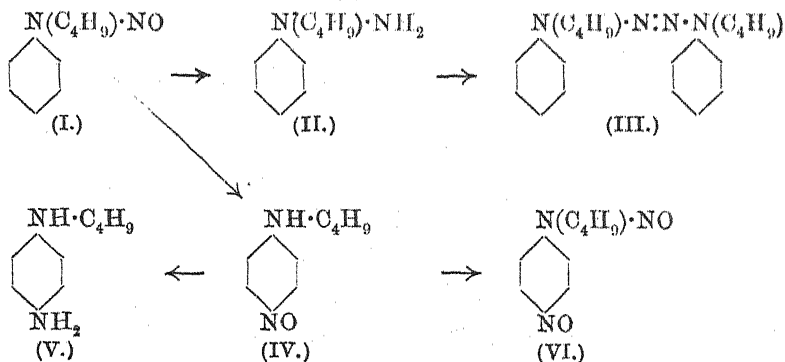
n-butylhydrazine (II), and this compound was then oxidised to diphenyldibutyltetrazone (III) by the action of yellow mercuric oxide in ethereal solution:

By means of Fischer and Hepp's reaction (*Ber.*, 1886, **19**, 2991; 1887, **20**, 1247) the nitrosoamine was converted into *p*-nitroso-*n*-butylaniline (IV). On keeping, the crude hydrochloride darkened, owing probably to the presence of free hydrogen chloride behaving similarly to *p*-nitroso*iso*butylaniline hydrochloride (Walker, *Annalen*, 1888, **243**, 298). *p*-Nitroso-*n*-butylaniline was easily reduced by means of zinc dust and hydrochloric acid to the corresponding diamine (V). The nitrosoamine is also decomposed into *p*-nitrosophenol and *n*-butylamine, thus confirming its constitution. It is converted into *p*-nitrosophenyl-*n*-butylnitrosoamine (VI) by the action of nitrous acid.

Whilst *p*-nitrosomethylaniline hydrochloride separated almost quantitatively in Fischer and Hepp's reaction (*loc. cit.*) from solution in a mixture of alcohol and ether, *p*-nitrosobutylaniline hydrochloride under similar conditions gave only a small precipitate (compare Walker, *Annalen, loc. cit.*). A yield equal to 75 per cent. of the weight of nitrosoamine taken is obtained by substituting a solution of hydrogen chloride in butyl alcohol for the ethyl-alcoholic solution and reducing the proportion of alcohol to ether by one-half.

p-Phenylene-*n*-butyldiamine resembled the other known monosubstituted *p*-phenylenediamines in being readily oxidised to *p*-benzoquinone and in yielding colour reactions with ferric chloride and nitrous acid (compare Fischer and Wacker, *Ber.*, 1888, **21**, 2614; Jacobson, *Annalen*, 1895, **287**, 131; Bamberger, *Ber.*, 1898, **31**, 1516; Bernthsen and Goske, *Ber.*, 1887, **20**, 929).

EXPERIMENTAL.

n-Butylaniline was prepared by heating one molecular proportion of aniline (93 grams) with slightly more than one molecular proportion of *n*-butyl chloride (100 grams) for thirty-six hours on a water-bath, using a reflux condenser. A crystalline deposit was produced which, after the liquid had been filtered off, was shown to be mainly aniline hydrochloride with a small amount of *n*-butylaniline hydrochloride. From the reddish liquid poured off the crystalline deposit, uncombined *n*-butyl chloride was removed by distillation and the residual oil treated with sodium hydroxide solution. The bases which separated were extracted with ether, the ethereal layer was left in contact with potassium carbonate for some time, and the solvent removed by evaporation; the oil obtained was then distilled.

At first, some *n*-butyl chloride mixed with aniline distilled over

below 180°.   The fraction 180—200° contained *n*-butylaniline mixed with aniline, and the distillate between 200° and 250° was *n*-butylaniline mixed with a smaller amount of aniline.   There was also a fraction boiling at 250—275°, which was found to consist chiefly of di-*n*-butylaniline; this was investigated later.   The distillate boiling at 200—250° on redistilling gave a large fraction at 240—245°, and by a further redistillation this gave a fraction boiling at 242—244°/765 mm.   By converting the latter fraction into the nitrosoamine and reducing with zinc dust and warm glacial acetic acid, *n*-butylaniline was obtained free from traces of the dialkyl compound.   It boiled at 241—242°/752 mm.   (Kahn gives 235°/720 mm.)

The fraction boiling between 200° and 250° from the original experiment with aniline and *n*-butyl chloride was not further fractionated for subsequent experiments, for the action of nitrous acid made it possible to separate the mono-*n*-butylaniline from aniline and di-*n*-butylaniline.   The fraction boiling between 200° and 250° (105 grams) was therefore dissolved in an excess of dilute hydrochloric acid, and a concentrated aqueous solution of sodium nitrite was slowly added until the yellow turbidity changed to red.   The nitrosoamine separated on top of the aqueous solution as a reddish-yellow oil, which was extracted with ether, the ethereal solution being washed with sodium hydroxide solution, and finally with water.   From the separated ethereal layer dried over potassium carbonate, the solvent was evaporated, leaving the nitrosoamine as a greenish-yellow oil.   From a portion (26·5 grams) of the oily fraction boiling between 200° and 250°, referred to above, 22 grams of phenyl-*n*-butylnitrosoamine were obtained.   This is insoluble in cold water, very sparingly so in hot water, soluble in strong acids, and in most organic solvents.   A fresh solution in acid is precipitated by sodium hydroxide solution.   The nitrosoamine is volatile in steam, collecting in the distillate as a pale yellow oil, heavier than water (compare Kahn, *loc. cit.*, p. 3367).

Both *n*-butylaniline and phenyl-*n*-butylnitrosoamine can be readily nitrated, yielding in each case yellow, crystalline nitro-compounds which are soluble in alcohol or acetone and insoluble in water, but can be recrystallised from concentrated nitric acid. They were not further investigated.

Phenyl-n-*butylhydrazine.*

Phenyl-*n*-butylnitrosoamine (20 grams) dissolved in glacial acetic acid (50 grams) was slowly added to zinc dust (100 grams), suspended in 200 c.c. of 90 per cent. alcohol, and the mixture was constantly stirred and kept at 10—20°.   When all the nitrosoamine

had been added, the mixture was heated to boiling and quickly filtered to prevent the deposition of crystals. The zinc dust was washed repeatedly with small quantities of warm absolute alcohol, the washings being added to the filtrate. This nearly colourless filtrate was rendered slightly acid by the addition of concentrated hydrochloric acid, and then evaporated to a small bulk. During the evaporation the solution gradually deepened in colour, until finally it became dark red. The concentrated solution of the hydrochloride was next treated with excess of concentrated sodium hydroxide solution until the precipitate first formed was completely redissolved. The crude base, which separated as a dark red oil, was extracted with ether, the ethereal layer dried over anhydrous potassium carbonate, and the solvent evaporated. The residual oil consisted chiefly of phenyl-n-butylhydrazine, together with some n-butylaniline. The yield of crude oil was usually 75—83 per cent. of the weight of phenyl-n-butylnitrosoamine used. In order to separate the n-butylaniline from the phenyl-n-butylhydrazine, the crude oil was dissolved in dry benzene and dry hydrogen chloride passed through the solution until there was no more absorption. The benzene solution at first changed to a deep red, but later it became paler in colour with the formation of a turbidity.

The benzene solution was filtered and evaporated to a small bulk, when the hydrazine was precipitated as a pale yellow crystalline mass on the addition of dry ether. By washing the precipitate with a small amount of benzene the hydrazine hydrochloride was dissolved, leaving behind the n-butylaniline hydrochloride. The phenyl-n-butylhydrazine hydrochloride was recovered from the benzene solution and twice more subjected to this treatment, when it was obtained pure. From chloroform the hydrochloride separated in white, needle-shaped crystals which are very readily soluble in water, benzene, chloroform, methyl or ethyl alcohols, and very sparingly so in ether or light petroleum (b. p. 60—80°). It reduces Fehling's solution on warming :

0·1030 gave 12·65 c.c. N_2 at 21·5° and 747·3 mm.* $N = 14·01$.
0·1244 ,, 0·0900 AgCl. $Cl = 17·90$.
$C_{10}H_{16}N_2,HCl$ requires $N = 13·96$; $Cl = 17·67$ per cent.

Treatment with sodium hydroxide solution and extraction with ether gave the base as an almost colourless oil. It boils at 247—250°/762·7 mm., decomposing slightly with the evolution of

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* In the nitrogen estimations recorded in this paper, the gas was measured over 40 per cent. potassium hydroxide solution. The pressures recorded have been corrected for vapour pressure of the potassium hydroxide solution.

ammonia.   Under diminished pressure the base can be distilled unchanged.

Diphenyldi-n-butyltetrazone.

The crude phenyl-*n*-butylhydrazine was dissolved in ether, and yellow mercuric oxide gradually added, following Fischer's method for the preparation of the tetrazone from phenylmethylhydrazine (*Annalen*, 1878, **190**, 108).   The red ethereal filtrate obtained on separation from the mercuric oxide and mercury was evaporated under diminished pressure, and on addition of aqueous alcohol the tetrazone was obtained in slightly yellow, flattened needles.   These crystals were dissolved in a small amount of aqueous alcohol (60 per cent.) and placed in a vacuum desiccator over calcium chloride until the tetrazone separated in white, shining plates melting at 72—73°. After melting and cooling, the melting point was again determined and found to be 73°.   On heating above its melting point, however, the compound gradually darkened, until at 110—120° there was an evolution of nitrogen, the liquid became dark brown, and did not solidify again on cooling:

0·0906 gave 13·22 c.c. N_2 at 14·7° and 758·5 mm. $N = 17·28$.

$C_{20}H_{28}N_4$ requires $N = 17·28$ per cent.

An   aqueous-alcoholic   solution   of   diphenyldi-*n*-butyltetrazone rapidly decomposed, the solution changing first to a mauve colour, then gradually to violet, and finally to blue and indigo.   The violet or blue solution was changed to an indigo colour by means of acids, and to a reddish-mauve colour having a blue fluorescence by alkalis, these changes being reversible.   Zinc dust and acetic acid destroyed the blue colour.   Concentrated nitric acid changed the colour to yellow, whilst aqueous iodine solution produced a dirty green coloration.   Lactic acid gave the indigo colour, which by the action of potassium iodide changed to olive green.   Dilute potassium permanganate was reduced.   The addition of bromine in carbon tetrachloride solution changed the indigo colour to a brownish-yellow.

p-*Nitroso-n-butylaniline.*

Phenyl-*n*-butylnitrosoamine was dissolved in about ten times its volume of dry ether, and four times its volume of alcoholic hydrogen chloride were added.   In a few minutes the green solution became red, and after some time small, brownish-red crystals of *p*-nitroso-*n*-butylaniline hydrochloride were deposited, which were collected, washed with alcohol, then ether, and dried.

It was found that *p*-nitroso-*n*-butylaniline hydrochloride was less readily soluble in *n*-butyl alcohol than in ethyl alcohol.   A butyl-alcoholic solution of dry hydrogen chloride was therefore used

instead of the ethyl-alcoholic solution. The nitrosoamine was dissolved in twice its volume of dry ether, and two volumes of a solution of dry hydrogen chloride in n-butyl alcohol were added. After two hours a copious yellow precipitate of the hydrochloride had formed, the deposition of which was accelerated by stirring. It was collected, washed with alcohol, and finally with ether.

To a solution of the hydrochloride in water an excess of ammonia was added, when the base was precipitated as a green, turbid oil which was extracted with ether. The ethereal extract of the nitroso-derivative was washed once with water and the ether evaporated, leaving the base as a green, dark liquid which solidified on cooling to a blue, shimmering mass. It was purified by dissolving in alcohol and adding water until a turbidity was produced. After some time the base crystallised in long, flattened needles melting at 58—59°:

0·1173 gave 16·32 c.c. N_2 at 22·0° and 742·7 mm. $N = 15·73$.

$C_{10}H_{14}ON_2$ requires $N = 15·76$ per cent.

By slow evaporation of the ethereal solution the compound crystallised in large steel-blue prisms. It is only sparingly soluble in water or light petroleum, but dissolves readily in ether, benzene, or alcohol. Concentrated solutions are green, whilst dilute solutions are yellow. The solid, although steel-blue when in crystalline form, is green or yellowish-green when powdered or crushed. The *hydrochloride* crystallises from a mixture of alcohol and ether in yellow needles, which are changed to red, and finally to a very dark colour, by traces of hydrogen chloride:

0·2386 gave 0·1588 AgCl. $Cl = 16·47$.

$C_{10}H_{14}ON_2,HCl$ requires $Cl = 16·52$ per cent.

It is very readily soluble in alcohol, water, or acetone, but insoluble in ether or light petroleum.

By the action of dilute nitric acid on the dilute aqueous solution of the hydrochloride, a yellow, crystalline nitro-compound was produced, insoluble in water, acid or alkali, but soluble in alcohol or ether. On crystallisation from hot aqueous alcohol it was obtained in long yellow needles, but was not further examined.

Decomposition of p-*Nitroso-*n-*butylaniline with Alkali.*

2·5 Grams of p-nitroso-n-butylaniline were added to 40 c.c. of a 10 per cent. solution of sodium hydroxide, and the mixture was distilled in a current of steam for twenty minutes, the distillate being collected in an excess of dilute hydrochloric acid. The reddish-brown residue was neutralised with dilute sulphuric acid until the colour became pale green, when the solution was extracted with

ether. On evaporation of the ethereal layer a pale buff-coloured residue was left, which dissolved in alcohol, acetone or ether to a green solution. By slow evaporation of the ether the compound was obtained in almost colourless needles melting and decomposing at 120—123°. It had the properties of *p*-nitrosophenol, and gave a red sodium salt, crystallising from water or from alcohol in red needles extremely readily soluble in water and sparingly so in ether or acetone. (Found, Na = 15·44. Calc., Na = 15·85 per cent.) The hydrochloric acid solution in which the distillate had been collected was evaporated to dryness, leaving an almost white residue, which was identified as *n*-butylamine hydrochloride by the analysis of the platinichloride. (Found, Pt = 34·87. Calc., Pt = 35·10 per cent.) The production of the primary aliphatic amine and *p*-nitrosophenol from the nitrosoamine proves that the nitroso-group, by the action of alcoholic hydrogen chloride, had migrated to the para-position, behaving in a manner similar to that observed when the lower alkyl derivatives of aniline, such as phenylmethylnitrosoamine, are similarly treated.

p-*Nitroso-n-butylanilinenitrosoamine.*

Two grams of *p*-nitroso-*n*-butylaniline hydrochloride were dissolved in a small amount of dilute hydrochloric acid, the solution was cooled in a freezing mixture, and a concentrated solution of sodium nitrite (a slight excess of 1 mol.) was added slowly. A greenish-yellow, flocculent precipitate separated, which was collected after an hour. It was purified by dissolving in alcohol and adding water until a turbidity was produced, and then leaving the mixture until crystallisation had taken place. The compound separated in small, green plates melting at 39·5°:

0·0855 gave 14·85 c.c. N_2 at 16·8° and 754·0 mm. N = 20·33.

$C_{10}H_{13}O_2N_3$ requires N = 20·29 per cent.

p-*Nitroso-n-butylanilinenitrosoamine* is freely soluble in most organic solvents, but almost insoluble in water. Dilute solutions become bright yellow by the action of alkalis, whilst acids almost discharge the colour, these changes being reversible. It was found that the colour of an alkaline solution could be discharged by the addition of one drop of $N/20$-sulphuric acid. The compound responded to Liebermann's test for nitroso-compounds.

p-*Phenylene-n-butyldiamine.*

Zinc dust (15 grams) was added gradually to a solution of *p*-nitroso-*n*-butylaniline hydrochloride (10 grams) in water, when a fairly vigorous reaction ensued, attended by evolution of heat, so

that it was necessary to cool the mixture. After the reaction had moderated, concentrated hydrochloric acid (45 c.c.) was gradually added and the mixture was heated for a short time on the water-bath until almost colourless. It was filtered hot from the excess of zinc dust, which was washed repeatedly with warm dilute hydrochloric acid and finally with alcohol. The acid filtrate was then evaporated to about half its bulk, rendered alkaline with sodium hydroxide solution, and the base which separated out as a dark-coloured oil was extracted with ether. p-*Phenylene*-n-*butyldiamine* was obtained in a pure condition by the addition of an excess of dilute sodium hydroxide solution to a concentrated aqueous solution of the hydrochloride cooled in ice. The base separated as a white, crystalline solid, which was collected and washed with water. On recrystallisation from light petroleum, it was obtained in white plates melting at 31·5°, having a pearly lustre. The colour slowly changed to red on exposure to air:

0·0631 gave 9·45 c.c. N_2 at 18·5° and 744·5 mm. N = 17·19.

$C_{10}H_{16}N_2$ requires N = 17·07 per cent.

An alternative method of obtaining the free base in a pure condition was also employed. The dark-coloured base was distilled instead of being converted into the hydrochloride. Under a pressure of 768 mm. it distilled over mainly at 302·5—303·5°, and on cooling solidified to a white, crystalline mass. It is readily soluble in most organic solvents, but moderately so in cold light petroleum, and insoluble in water.

p-*Phenylene*-n-*butyldiamine dihydrochloride* crystallised from hot absolute alcohol in small, glistening plates which did not melt at 200°:

0·0750 gave 7·80 c.c. N_2 at 20° and 746·3 mm. N = 11·90.

0·1324 „ 0·1610 AgCl. Cl = 30·08.

$C_{10}H_{16}N_2,2HCl$ requires N = 11·82; Cl = 29·90 per cent.

It is insoluble in ether, sparingly soluble in cold absolute alcohol, more readily so in hot alcohol, and very readily soluble in water. With a small amount of ferric chloride solution, a neutral solution of the hydrochloride gave a dirty green coloration which changed slowly through a succession of colours to a dark red. The green colour was restored on adding more ferric chloride. With potassium ferrocyanide the hydrochloride solution became olive-green, changing to blue on the addition of alkali. Oxidation by boiling with ferric chloride or potassium dichromate and dilute sulphuric acid produced an odour resembling that of p-benzoquinone. A solution of bromine in aqueous potassium bromide gave a yellow precipitate which gradually darkened on keeping.

Diazotisation of p-Phenylene-n-butyldiamine Dihydrochloride.

To an aqueous solution of the hydrochloride (1 mol.) rendered acid by the addition of hydrochloric acid (3 mols.) and cooled in a freezing mixture, an aqueous solution of sodium nitrite was added until there was a slight excess of nitrous acid present. On first adding the sodium nitrite the hydrochloride solution became green and then rapidly turned to a brown tint. *p*-Aminodiphenylamine behaves in a somewhat similar manner (Jacobson, *loc. cit.*). On adding this diazotised solution to an aqueous solution of platinic chloride, a light yellow precipitate of the diazonium *platinichloride* was obtained, which was collected and washed well with water and finally with alcohol and ether:

0·1888 gave 17·50 c.c. N_2 at 12° and 758·7 mm.   N = 11·08.
0·1509 ,, 0·0381 Pt.   Pt = 25·25.
   $(C_{10}H_{14}N_3Cl)_2PtCl_4$ requires N = 11·05 ; Pt = 25·66 per cent.

This salt was almost insoluble in water, but sparingly so in alcohol. It commenced to darken at 115—120°, and decomposed at 147—150° with a brisk evolution of nitrogen. When heated suddenly in a Bunsen flame it decomposed explosively.

On the addition of an aqueous solution of the diazonium chloride, freed from nitrous acid by means of carbamide, to an alkaline solution of β-naphthol, an azo-compound separated as a red, crystalline powder, which was collected after a few hours. In the dry condition it is almost black and has a metallic lustre. It is insoluble in water, but soluble in most organic solvents, and dissolves in concentrated sulphuric acid, giving a deep red colour. An acetylacetone derivative was obtained as an orange precipitate on adding a solution of the diazotised *p*-diamine, free from nitrous acid, to an alcoholic solution of acetylacetone. On the addition of sodium acetate there was a yellow turbidity, from which crystals soon separated. The compound crystallised from aqueous alcohol in yellow needles, but was not further examined.

XC.—*The Limitations of the Balance.*

By BERTRAM BLOUNT.

ABOUT three years ago the author had occasion, in the course of a research, to make accurate weighings extending over some months. The balances used were by the first makers, and the discrepancies observed were at first attributed to the errors of experiment arising from the difficulties of the research. Slowly and reluctantly, however, the conclusion was drawn that the errors lay in the balances themselves, and the following is an account of the nature and extent of these errors.

It is usually accepted that a good balance carrying 200 grams in each pan should turn with certainty with 0·1 milligram, an accuracy of one part in two millions. Much higher accuracies have been claimed, but for the purpose of the research in question this degree of accuracy was sufficient. It was assumed that it could be obtained without difficulty, and the research was started on this assumption. As has been mentioned above, the cause of the error was not at first suspected, and after many months of work the balances themselves were critically tested. It may be stated at once that all were usually accurate over a short period of a few hours or even a few days, but over longer periods of a few weeks or months they showed themselves untrustworthy.

In all, six balances were used, three being provided by the kindness of Professor Pope at Cambridge; the other three were at the laboratory in the author's house.

Those at Cambridge were a Sartorius carrying 200 grams in each pan, a smaller Sartorius carrying 100 grams in each pan, and a Bunge, preferred by the late Prof. Ewing for his own work, carrying 100 grams in each pan.

Those in London were an Oertling carrying 200 grams in each pan (and it may be remarked that the beam used was selected out of five by the makers as the best they had), another Oertling with a load of 100 grams, and a modern Bunge carrying 200 grams.

Each balance could be read with accuracy to 0·1 milligram, and in all cases standard weights were used.

All proper precautions were taken to secure uniformity of condition.

Four of the balances were used in their own case, one in a massive gun-metal case, which was air-tight, and one in an all-glass case, which was also air-tight.

In each case twin weights were used so as to prevent errors creeping in from this cause.

Weighings were made by three independent observers at both Cambridge and London, and as there were far too many to record in full in a short paper, only those representing the maximum variations are recorded, and are as follows:

CAMBRIDGE.

Small Sartorius.

Date	Left	Right	Temp.	Tenths mg.	Date	Left	Right	Temp.	Tenths mg.
29.4.17	7	6¾	15·5°	+0·25	25.6.17	3*	3†	17·5°	± 0
30.4.17	7	7	15	± 0	29.6.17	4¼	5	17*	-- ¼
5.5.17	7	8½	15	1½	4.7.17	4½	5	16·5	-- ¼
5.5.17	5	5½	15	-- ¾	5.7.17	4	3½	16·5	+¼
6.5.17	2¼	2	14	+½	7.7.17	4	3	17	+1
7.5.17	2	2	14	± 0	9.7.17	6	6½	16·5	-- ½
11.5.17	4	5½	14	-- 1½	12.7.17	4½	4½	16·5	± 0
18.5.17	4	7	14·5	-- 3	15.7.17	5	4†	18	+1
27.5.17	3	3½	17	-- ½	19.7.17	6¼	7	18	-- ¼
29.5.17	7	7	17	± 0	20.7.17	7	6½	18	+½
31.5.17	3½	2¼	17·3	+1	29.7.17	4	2	19·5	+2
4.6.17	8½	7½	17	+1	1.8.17	7	7	17·7	± 0
10.6.17	6½	5	17·5	+1½	6.8.17	7½	9	17·5	-- 1½
14.6.17	4†	4	18	± 0	11.8.17	3½	3	17·5	+½
15.6.17	7	5½	18·5	+1½	13.8.17	5	5½	18	-- ½
17.6.17	4	3	19	+1	20.8.17	3*	2½	17·5	+½
21.6.17	6	3*	19	+3	30.8.17	7	8†	16·5	-- 1
22.6.17	6	3†	18·5	+3					

Greatest difference in 4 months, 0·6 milligram.

* Full.   † Bare.

Bunge.

Date	Left	Right	Temp.	Tenths mg.	Date	Left	Right	Temp.	Tenths mg.
29.4.17	4	4†	15·5°	+0	12.7.17	9	8	16°	+1
30.4.17	5	5*	15	+0	12.7.17	2	5	16	-- 3
30.4.17	5½	5	15·5	+½	12.7.17	2	2	16·5	+0
2.5.17	7	5½	14	1½	13.7.17	7	5	16*	+2
2.5.17	2½	3	14·5	-- ½	13.7.17	4	5	16·5	-- 1
7.5.17	7	6	13·5	+1	13.7.17	2	2	16·5	+0
10.5.17	4½	6	13	-- 1½	13.7.17	1	3	16·5	-- 2
11.5.17	5	4½	14	+½	17.7.17	3	3	17·3	+0
12.5.17	2	3	14	-- 1	20.7.17	1½	3	18	-- 1½
22.5.17	7	7	15·5	± 0	29.7.17	5	5	19	± 0
24.5.17	6	7	15·7	-- 1	3.8.17	5½	6	17	-- ½
31.5.17	6	5	17	+1	12.8.17	6	5	17·7	+1
1.6.17	3	4	17	-- 1	18.8.17	3	5†	17·5	-- 2
3.6.17	6	5	17	+1	20.8.17	5½	4	17	+1½
11.7.17	7	7½	15	-- ½	30.8.17	7	8	16	-- 1

Greatest difference in 4 months, 0·5 milligram.

* Full.   † Bare.

Large Sartorius.

Date.	Divisions. Left.	Right.	Temp.	Tenths mg.	Date.	Divisions. Left.	Right.	Temp.	Tenths mg.
29.4.17	7	7	15·5°	± 0	28.6.17	9	10	17°	— 1
30.4.17	5	6	15·5	— 1	5.7.17	9	10	16	— 1
1.5.17	6	9	14·5	— 3	6.7.17	6	8	16	— 2
1.5.17	3½	7	15	— 3½	12.7.17	1	4	16·5	— 3
4.5.17	6	6	14·5	± 0	13.7.17	5½	7½	16·5	— 2
7.5.17	4½	6	13·5	— 1½	19.7.17	9	9*	18	± 0
10.5.17	6	6½	13	— ½	23.7.17	7	8*	18	— 1
12.5.17	2½	4	14	— 1½	26.7.17	5	5	19	± 0
13.5.17	9	9½	15	— ½	29.7.17	8½	8	19	+ ½
14.5.17	8	9½	15	— 1½	1.8.17	9	8	17	+ 1
26.5.17	6½	7	16	— ½	2.8.17	4*	3	17	+ 1
28.5.17	9	10	16·75	— 1	4.8.17	10	7†	17	+ 3
29.5.17	6	6	16·25	± 0	6.8.17	9½	3	17	+ 6½
7.6.17	{4½, 4	6, 5}	17	{— 1½, — 1}	9.8.17	12	3†	17	+ 9
14.6.17	7†	7	18	± 0	11.8.17	12	1	17·5	+11
17.6.17	9	9½	18·75	— ½	13.8.17	12	— 1	17	+13
18.6.17	5	4½	19	+ ½	19.8.17	12*	— 6	17	+18
19.6.17	9	9	19	± 0	21.8.17	12	— 7	17	+19
22.6.17	9	10	18	— 1	25.8.17	12	— 8	17	+20
26.6.17	3	5	17	— 2	31.8.17	12*	—11	16	+23
					1.9.17	13	—11	16	+24

Greatest difference, 2·5 milligrams in 4 months.
Rejecting the readings after 4.8.17, 0·45 milligram in 3 months.

* Full. † Bare.

LONDON.

Large Oertling.

Date.	Divisions. Left.	Right.	Temp.	Tenths mg.	Date.	Divisions. Left.	Right.	Temp.	Tenths mg.
14.6.17	4	4	24·5°	± 0	26.7.17	0	3½	22°	— 7
19.6.17	4½	7½	21·9	— 6	7.8.17	1	9	20·3	—16
23.6.17	3	3	16·3	± 0	4.9.17	3½	6	20·3	— 5
3.7.17	5	7	18·2	— 4	10.9.17	1	7	20·4	—12
7.7.17	3	3½	16·7	— 1	14.9.17	1	5	18	— 8
20.7.17	2	7	21·3	—10					

Greatest difference in 3 months, 1·6 milligrams.

Bunge.

Date.	Divisions. Left.	Right.	Temp.	Tenths mg.	Date.	Divisions. Left.	Right.	Temp.	Tenths mg.
14.6.17	4	4	24°	± 0	4.8.17	6	9½	16·5°	— 7
15.6.17	1	3	19·5	— 4	5.8.17	3	8	18	—10
16.6.17	2	3	21·5	— 2	8.8.17	6½	8½	19·5	— 4
30.6.17	3	8	13·5	—10	20.8.17	4	4½	18·5	— 1
10.7.17	7	10½	16	— 7	22.8.17	7½	6¼	20·5	+ 2
14.7.17	6	6½	22	— 1	26.8.17	5	8	18	— 6
16.7.17	3	5½	20	— 5	6.9.17	6½	7½	20	— 2
26.7.17	2	1	21·5	+ 2	9.9.17	0	2	20	— 4
27.7.17	1	2½	21	— 3	13.9.17	5	8	17	— 6
2.8.17	1½	6	15·5	— 9					

Greatest difference in 3 months, 1·2 milligrams.

Small Oertling.

Date.	Divisions.		Temp.	Tenths mg.	Date.	Divisions.		Temp.	Tenths mg.
	Left.	Right.				Left.	Right.		
14.6.17	5	5	24°	+ 0	1.8.17	2½	3	16°	− 1
30.6.17	3½	2	14	+ 3	2.8.17	4½	3½	16·5	+ 2
27.7.17	6½	6½	22·2	+ 0	8.8.17	2½	2½	20·5	+ 0
31.7.17	2	1	17·2	+ 2	10.8.17	2	2	19	

(From 16.8.17 to 22.8.17 balance remained constant (left and right equal) with variations of temperature of 3°.)

(From 6.8.17 to 1.9.17 the balance did not vary more than ¼ division with variations of temperature of 4·2°.)

1.9.17	3½	2¼	19	+ 2	14.9.17	9	8¼	18·3	− 1
6.9.17	2¼	2¼	21	+ 0					

Greatest difference in 3 months, 0·4 milligram.

These figures show that six balances of the best make, observed by three people at two different places, gave a variation over as short a period as four months varying from 0·4 to 1·6 milligrams, and that these variations cannot be correlated with any variation of external conditions.

The author is well acquainted with earlier work by Poynting and others, and does not doubt that accurate readings can be made over a short period, but finds that constancy cannot be relied on over as short a period as four months.

The natural suggestion of the cause of discrepancy is that there is a difference of temperature between the two arms of the beam. This has been dispelled by direct observation. Two thermometers reading to 0·01° were placed one on each pan of a balance in the same room as that containing the three balances used in London. Except in one instance, when by accident direct sunlight fell on the bulb of one thermometer, no greater difference than 0·02° was observed. Calculations, confirming those of Landolt, show that such a difference of temperature in the beam itself is negligible in its effect on the indications of the balance, and this difference, which represents that of the pans, is far greater than would be possible in a solid piece of metal, like a beam under normal conditions. As the fact remains that these variations occur, however, there clearly must be a physical cause. The matter has been referred to engineers of eminence, accustomed to consider stresses, and one was so good as to compute the stresses in a beam identical with that of two of the balances. He reported that the beam was amply strong to carry a load without flexure, although condemning the design as clumsy. The slow flow of metals under stress is well known, and might provide an explanation were it not that the

beam of a balance is not under stress except in the short time of weighing. Moreover, some permanent set in one direction or the other might be expected.

It remains to consider other probable causes of the inconstancy observed.

There may be an alteration in the effective length of the two arms of the balance. In the case of the six balances examined, two had their end knife-edges set in sealing-wax, two were held by set screws, and the other two were apparently pressed in. In all three methods of construction, fortuitous movement of the knife-edge is easily conceivable, and to this explanation the author inclines.

As a balance of the best make is generally regarded as capable of use to its assigned limit of accuracy, chemists generally have accepted its indications without question. The present inquiry, which only arose out of the main research, shows that this view is untenable if constant readings are to be expected over a relatively short time. Nor is there any indication as to when the variations may occur. As many chemical and physical experiments are necessarily lengthy, an unsuspected alteration of the indications of the balance may in the past have led to grave errors. It seems to be incumbent on balance makers to provide an instrument capable of carrying 200 grams in each pan turning with certainty to 0·1 milligram, and dependable in this respect for a reasonable time—say a year—without alteration or readjustment, it being always understood that all proper care is taken in using the instrument. At the time of writing, it appears that such a balance does not exist.

76, York St.,
    Westminster, S.W.   [*Received, October 25th*, 1917.]

XCI.—3 : 4-*Di*-p-*nitrotetraphenylfuran*.

By Arthur Gordon Francis.

The formation of furan derivatives by the condensation of benzoins has been observed by several workers. Zinin (*Zeitsch. für Chemie*, 1867, [ii], **3**, 313), by the action of concentrated hydrochloric acid at 130° on benzoin, obtained lepiden, benzil, and an oil. Limpricht and Schwanert (*Ber.*, 1871, **4**, 337) showed that dibenzoylstilbene (Zinin's acicular oxylepiden) is obtained by digesting benzoin with dilute sulphuric acid, and that when heated with benzoin it yields lepiden and benzil. On reduction, dibenzoylstilbene yields bidesyl.

Magnanini and Angeli (*Ber.*, 1889, **22**, 855) showed that when bidesyl is heated with concentrated hydrochloric acid at 130—140° for two hours, lepiden is formed. Dorn (*Annalen*, 1870, **153**, 358) suggested, and Japp and Klingemann (T., 1890, **57**, 662) showed, that lepiden is tetraphenylfuran. Japp and Tingle (T., 1897, **71**, 1138) proposed the formula:

$$\text{CPh}\!=\!=\!=\!\text{CPh}$$
$$\text{CPh}\!<\!{}^{O}_{O}\!>\!\text{CPh},$$
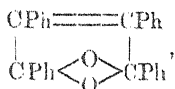
for dibenzoylstilbene.

The relation of these compounds is shown in the following scheme:

Benzoin.   Bidesyl.   Dibenzoylstilbene.

CHPh·OH   CHPh·CHPh   CPh====CPh
COPh   COPh COPh   CPh$<$${}^{O}_{O}$$$>$CPh

HCl   HCl   Benzoin

CPh—CPh
CPh CPh
\/
O

Lepiden or tetraphenylfuran.
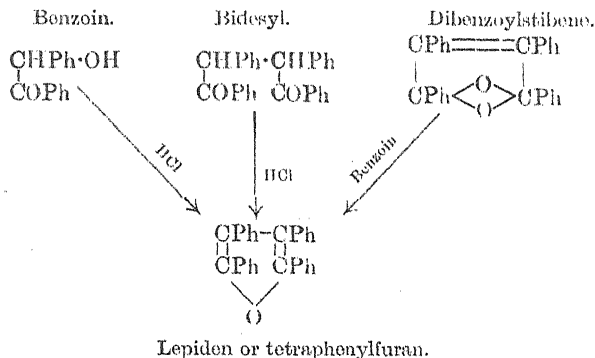
More recently Irvine and McNicoll (T., 1908, **93**, 950, 1601) have shown that methoxyfuran derivatives can be obtained by the action of hydrochloric acid in methyl-alcoholic solution on benzoin, anisoin, and furoin, but that when ethyl alcohol is substituted for methyl alcohol no such condensation products are formed, only the ethyl ester being obtained, as is usual in the Fischer esterification process.

The author and Keane (T., 1911, **99**, 344) described p-nitro-acetylbenzoin, and attempted to hydrolyse this substance and also the nitrobenzoylbenzoin prepared by Zinin (*Annalen*, 1857, **104**, 116). Zinin states that the position of the nitro-group in nitro-benzoylbenzoin was not determined. This compound is now shown to be p-nitrobenzoylbenzoin, $NO_2 \cdot C_6H_4 \cdot CHBz \cdot OBz$, by the same methods that fixed a similar constitution for p-nitroacetylbenzoin (*loc. cit.*).

Both p-nitroacetylbenzoin and p-nitrobenzoylbenzoin yield, on hydrolysis with hydrochloric acid under appropriate conditions, the same condensation product, together with p-nitrobenzil. The reaction is quantitative, and for every three molecules of nitroacyl-

benzoin used, one molecule of the condensation product and one molecule of *p*-nitrobenzil are formed. This condensation product is shown to be 3:4-*di*-p-*nitrotetraphenylfuran*. The probable course of the reaction may be stated as follows:

(1) The nitroacylbenzoin is first hydrolysed:

$$NO_2 \cdot C_6H_4 \cdot CHBz \cdot OBz(Ac) \longrightarrow NO_2 \cdot C_6H_4 \cdot CHBz \cdot OH.$$
(I.)
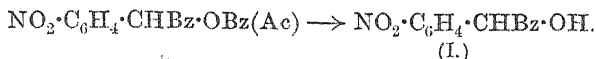
(2) Two molecules of the nitrobenzoin thus formed are condensed and reduced to dinitrobidesyl by a third molecule of nitrobenzoin, which is itself oxidised to *p*-nitrobenzil:

$$NO_2 \cdot C_6H_4 \cdot CHBz \cdot OH$$

$$NO_2 \cdot C_6H_4 \cdot CHBz \cdot OH \qquad\qquad HO \cdot CHBz \cdot C_6H_4 \cdot NO_2$$

$$NO_2 \cdot C_6H_4 \cdot CHBz \cdot CHBz \cdot C_6H_4 \cdot NO_2 + NO_2 \cdot C_6H_4 \cdot COBz$$
(II.)
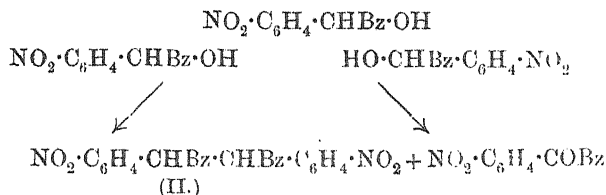
(3) The dinitrobidesyl under the influence of hydrochloric acid loses water and is converted into dinitrotetraphenylfuran:

$$NO_2 \cdot C_6H_4 \cdot \underset{COPh}{CH} \text{---} \underset{COPh}{CH} \cdot C_6H_4 \cdot NO_2 \longrightarrow$$

$$NO_2 \cdot C_6H_4 \cdot \underset{CPh \cdot OH}{C} \text{------} \underset{CPh \cdot OH}{C} \cdot C_6H_4 \cdot NO_2 \longrightarrow NO_2 \cdot C_6H_4 \cdot \underset{CPh}{C} \text{---} \underset{CPh}{C} \cdot C_6H_4 \cdot NO_2$$
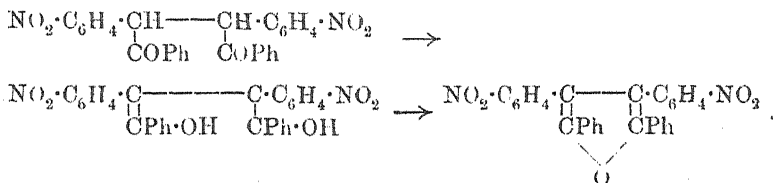
From this view of the course of the reaction the constitution of the condensation product is regarded as 3:4-di-*p*-nitrotetraphenyl-furan. The intermediate compounds *p*-nitrobenzoin (I) and dinitro-bidesyl (II) have not as yet been obtained, although attempts were made to isolate them by partial hydrolysis by means of hydrochloric acid and water.

The investigation is accordingly incomplete in this respect, but the results obtained so far are published, as the author is likely to be prevented by pressure of other work from continuing the research for some time to come.

EXPERIMENTAL.

Hydrolysis of p-*Nitroacetylbenzoin.*

Forty grams of *p*-nitroacetylbenzoin melting at 125° (uncorr.) were dissolved in 500 c.c. of boiling 90 per cent. alcohol in a capacious flask fitted with a reflux condenser. When completely dis-

solved, 30 c.c. of concentrated hydrochloric acid (D 1·16) were added slowly through the condenser, so as not to stop the ebullition of the liquid. At the end of half an hour, yellow needles began to be deposited. After six hours a voluminous mass of crystals had separated, and the solution had a strong odour of ethyl acetate. It was then filtered while boiling and washed several times with boiling 90 per cent. alcohol to remove *p*-nitrobenzil. The crude product melted at 207° (uncorr.), and after recrystallisation from glacial acetic acid the pure substance (21 grams) melted at 211° (uncorr.). From the alcoholic solution 10 grams of *p*-nitrobenzil were recovered.

3:4-*Di*-p-*nitrotetraphenylfuran* crystallises from glacial acetic acid in long, pale yellow, silky needles. It is very sparingly soluble in light petroleum, ether, cold or hot 90 per cent. alcohol, or water, and moderately so in benzene, toluene, acetone, or chloroform. It crystallises best from acetic anhydride or glacial acetic acid. One gram dissolves in 50 c.c. of boiling glacial acetic acid :

0·1002 gave 0·2672 CO_2 and 0·0357 H_2O.   C = 72·72; H = 3·95.

0·2744   ,,   15·0 c.c. N_2 (moist) at 19° and 748·5 mm.   N = 6·28.

0·3384, in 17·677 benzene, gave E = 0·12°.   M.W. = 426.

$C_{28}H_{18}O_5N_2$ requires C = 72·73; H = 3·90; N = 6·06 per cent.

M.W. = 462.

Action of Alcoholic Hydrogen Chloride at 42° on p-Nitroacetyl-benzoin.

Two grams of *p*-nitroacetylbenzoin were heated with 150 c.c. of absolute alcohol saturated with dry hydrogen chloride in a thermostat at 42° for four hours. After some time a yellow solid separated, which on crystallisation from glacial acetic acid melted at 210° and was dinitrotetraphenylfuran.

From the portion soluble in alcohol only *p*-nitrobenzil, melting at 140°, could be isolated, together with unchanged nitroacetyl-benzoin.

Action of Water on p-Nitroacetylbenzoin.

Five grams of nitroacetylbenzoin were heated with 10 c.c. of water at 180° for six hours. No pressure was observed on opening the tube. The aqueous layer was decanted through a filter and was found to contain acetic acid. The solid product was a red resin; from which *p*-nitrobenzil melting at 140° and *p*-nitrobenzoic acid melting at 238° were isolated. No dinitrotetraphenylfuran was isolated, nor could any intermediate product be obtained.

Constitution of Nitrobenzoylbenzoin

Nitrobenzoylbenzoin was prepared by Zinin's method (*loc. cit.*). The specimen melted at 137° (uncorr.). (Found, N = 4·3. Calc., N = 3·9 per cent.)

When hydrolysed and oxidised by nitric acid (D 1·4) it yields benzoic acid and *p*-nitrobenzil. When oxidised with a mixture of sulphuric acid (20 c.c. of concentrated sulphuric acid in 20 c.c. of water) and an approximately normal solution of potassium dichromate, as described for *p*-nitroacetylbenzoin (*loc. cit.*), it yields benzoic acid and *p*-nitrobenzoic acid. The constitution,

$$(4)NO_2 \cdot C_6H_4(1) \cdot CHBz \cdot OBz,$$
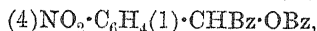
similar to that of *p*-nitroacetylbenzoin, is therefore deduced. These reactions take place with more difficulty than in the case of *p*-nitroacetylbenzoin.

Hydrolysis of p-Nitrobenzoylbenzoin.

(1) Five grams of *p*-nitrobenzoylbenzoin melting at 137° were heated under reflux with 150 c.c. of ethyl alcohol and 7 c.c. of aqueous hydrochloric acid (D 1·16). At the end of two and a-half hours there was no separation of yellow needles, no yellow colour in the solution, and no odour of ethyl benzoate. The *p*-nitrobenzoyl-bezoin was recovered unchanged.

(2) Four grams of *p*-nitrobenzoylbenzoin were heated under reflux for twenty-four hours with a mixture of equal parts of aqueous hydrochloric acid (D 1·16) and amyl alcohol, more acid being added from time to time. The insoluble product weighed 2·2 grams. After crystallisation once from toluene and twice from glacial acetic acid, there remained 1·5 grams of dinitrotetraphenyl-furan melting at 210°. When mixed with dinitrotetraphenylfuran melting at 211°, obtained by the hydrolysis of *p*-nitroacetylbenzoin, the mixture melted at 210°. The substances were therefore identical.

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XCII.—*The " Uniform Movement" during the Propagation of Flame.*

By Walter Mason and Richard Vernon Wheeler.

The initial slow propagation of flame that takes place when an inflammable mixture at rest is ignited at a point, is usually regarded as controlled by the transference by conduction of the heat developed by the combustion of the mixture immediately surrounding the point of ignition, whereby successive contiguous portions of the mixture are raised in temperature until chemical action becomes rapid. The initial speed of propagation of flame in a given mixture away from the point of ignition should mainly depend, according to this view, (1) on the conductivity for heat of the unburnt mixture, and (2) on the velocity with which a moderately heated layer begins to react chemically and so to rise gradually in temperature, or, in other words, on the rate of change of reaction velocity with temperature.

Under certain conditions, with all inflammable mixtures of gases and air at atmospheric temperature and pressure, the initial slow propagation of flame can be maintained at a uniform speed over a considerable distance of travel from the point of ignition. The conditions most favourable, or necessary, to obtain and maintain this " uniform movement " of flame are that the inflammable mixture should be contained in a long, straight, and horizontal tube open at one end and closed at the other; and that ignition should be effected at the open end of the tube by a source of heat not greatly exceeding in temperature the ignition-temperature of the mixture, and not productive of mechanical disturbance of the mixture. The speed of the uniform movement then depends on the composition of the mixture (presumed to be at atmospheric temperature and pressure), and on the diameter of the tube in which it is contained (see p. 1051); above a certain (small) diameter the material of which the tube is made does not appreciably affect the speed of the flame. With a tube of given diameter the speed of the uniform movement of flame in a mixture can be regarded as a definite physical constant for that mixture.

Following Vicaire (*Ann. Chim. Phys.*, 1870, [iv], **19**, 118), Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], **4**, 274) put forward theoretical considerations respecting the transference of heat during the burning of gaseous mixtures, from which it should be possible to deduce the speed of the flame during the uniform movement, as follows.

Suppose the flame to be propagated in a tube of uniform cross-section filled with the combustible mixture at an initial temperature θ. At a given moment during the propagation the "layer," A (Fig. 1), becomes inflamed. The mass of burnt gases which fills the tube behind A is at a temperature T, the "combustion-temperature," which can be calculated. The layer of gas immediately in contact with A and in front of it is at the ignition-temperature, t, of the mixture, or, rather, at a temperature infinitely close to t. The successive layers in front are at temperatures gradually decreasing from t to θ. The layer A itself must be at a temperature, T', higher than T, for at the moment when it was inflamed it had already been raised to t. If we neglect the variation in the specific

<p align="center">Fig. 1.</p>
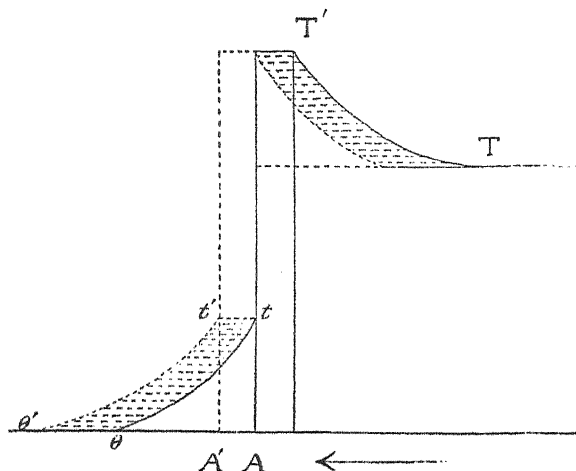
heats of the gases between T and T', and assume $\theta = 0$, then $T' = T + t$.

At the moment of inflammation of the layer A, of thickness ds, the distribution of temperatures in the tube can be represented as in Fig. 1, in which beyond A a gradual levelling of temperature from T' to T is shown. At the end of an infinitely short time, $d\tau$, the layer A', of thickness ds next to the layer A, becomes inflamed in its turn and the whole diagram advances through a distance ds. For this to take place the front part of the tube must gain a quantity of heat represented by the infinitely small area $tt'\theta\theta'$, which is equal to the rectangle $AA'tt'$. This quantity of heat is that necessary to raise the temperature of the layer of thickness ds from θ to

t; it is therefore equal to $c'(t-\theta)ds$, c' being the specific heat of the burning or just burnt gases.

The quantity of heat lost by the hinder part of the tube must balance that gained by the front part. Now the layer A that gives up its heat in front is at a temperature T', and is between a layer at a temperature t and one at T. The quantity of heat given up by A in unit time will therefore be a function of T and t, and can be stated thus:

$$c'(t-\theta)ds = d\tau F(T,t),$$

whence we obtain for the speed of propagation of flame:

$$v = ds/d\tau = F(T,t)/c'(t-\theta) \quad . \quad . \quad . \quad . \quad (1).$$

The exact form of the function $F(T,t)$ cannot readily be determined. However, one can presume that it is proportional to the conductibility, L, of the unburnt gas; and one can state that it becomes zero when $T=t$ and for that value of T only. It would seem that when the temperature of combustion, T, exceeds the temperature of inflammation, t, the heat necessary for the inflammation of a layer can be transmitted integrally. We can therefore put the expression for v in the form:

$$v = \frac{L(T-t)}{c'(t-\theta)} \cdot F'(T,t) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and it may be that $F'(T,t)$ is a constant.

The only point open to criticism in this otherwise lucid reasoning is that which attributes to the "layer" of gas that is actually burning a higher temperature (T') than it would attain if it burned without previous heating to its ignition-temperature (t). Mallard and Le Chatelier found confirmation of this view in the observation by Gouy (*Ann. Chim. Phys.*, 1879, [v], **18**, 1) that, as judged from photometric measurements, the surface of the bright green inner cone of a Bunsen flame is the hottest part of the flame; for the surface of this inner cone is the "burning layer" of a stationary explosion, the rate of propagation of flame downwards in the mixture being equal to the rate of flow of the unburnt gases upwards. Gouy showed that there is a simple relation between the area of surface of the inner cone, the rate of flow of the mixture, and the speed of propagation of flame therein; and Michelson (*Ann. Phys. Chem.*, 1889, [iii], **37**, 1), who adopted *in toto* Mallard and Le Chatelier's theoretical considerations, and at a later date Mache (*Ann. Physik.*, 1907, [iv], **24**, 527) used this relation to determine the "normal" speed of propagation of flame in a number of gaseous mixtures.

Haber and Richardt (*Zeitsch. anorg. Chem.*, 1904, **38**, 5), however, showed by actual thermo-electrical measurements that the

surface of the inner cone of a Bunsen flame is not the hottest part of the flame, and concluded that its brightness is a phenomenon of luminescence.   Further, they denied the possibility of the burning layer during the uniform movement in the propagation of flame along a tube attaining a higher temperature than it would if it were heated merely by its own heat of radiation, for the reason that while it is burning it must lose to successive layers as much heat as it gained from earlier burnt layers. Haber and Richardt's argument is summarised in the following quotation from their paper (p. 55):

" Die Vorwärmung eines explosiblen Gasgemenges erhölt die Verbrennungstemperatur, wenn sie auf Kosten der Wärme des *verbrannten* Gases erfolgt (Regenerativsystem, Öfen der Gasanstalten u.s.w.), aber sie erhölt sie nicht, wenn sie auf Kosten der Wärme des *verbrennenden* Gases erfolgte (Flamme, Explosion), denn da das Gebilde, welches die Vorwärmung bewirkt, soviel Wärme abgibt, als das vorgewärmte aufnimmt, so kann Temperatursteigerung durch Vorwärmung nur eintreten, wenn die Wärmeabgabe dem Temperaturansteig zeitlich nachfolgt und nicht, wenn sie ihn begleitet."

We consider Haber and Richardt's view to be the correct one. Mallard and Le Chatelier's equation (2) is, however, affected only as regards the magnitude of the function $F(T,t)$, which is, in any event, indeterminate.   The important deduction from the equation is that, in mixtures that have the same conductibility for heat, the speed of the flame during the uniform movement should be directly proportional to $T - t$, and inversely proportional to $t - \theta$.

The effect of variation in the conductibility of the mixture on the speed of the uniform movement of flame is well shown with mixtures of hydrogen and air (Haward and Otagawa, T., 1916, **109**, 85).   The fastest speeds are obtained with mixtures containing from 38 to 45 per cent. of hydrogen instead of with the mixture that contains hydrogen and oxygen in combining proportions and has the highest temperature of combustion.   The thermal conductivity of hydrogen is 31.9×10^{-5}, compared with that of air, 5.22×10^{-5}, and, as already stated, the mixtures in which the speeds of the flames are fastest contain between one-third and one-half their volume of hydrogen.   When the combustible gas has a thermal conductivity more nearly approaching that of the air with which it is mixed, and when it forms but a small proportion of the mixture, as with methane, the influence of thermal conductivity on the speed of propagation of flame can be neglected or regarded as constant.

If c' also be regarded as constant over the range of temperatures

concerned, the speed of the uniform movement of flame in mixtures such as those of methane with air should be proportional to $T - t/t - \theta$, if the uniform movement truly represents the transference of heat by conduction. In order to obtain data whereby to test this conclusion, and to elucidate the nature of the physical constant which we regard the uniform movement of flame to be, we have determined the speeds (in a tube 5 cm. in diameter) in a number of mixtures of methane, oxygen, and nitrogen, of which we have also determined the relative ignition-temperatures and of

Fig. 2.

Methane. Per cent. of mixture.
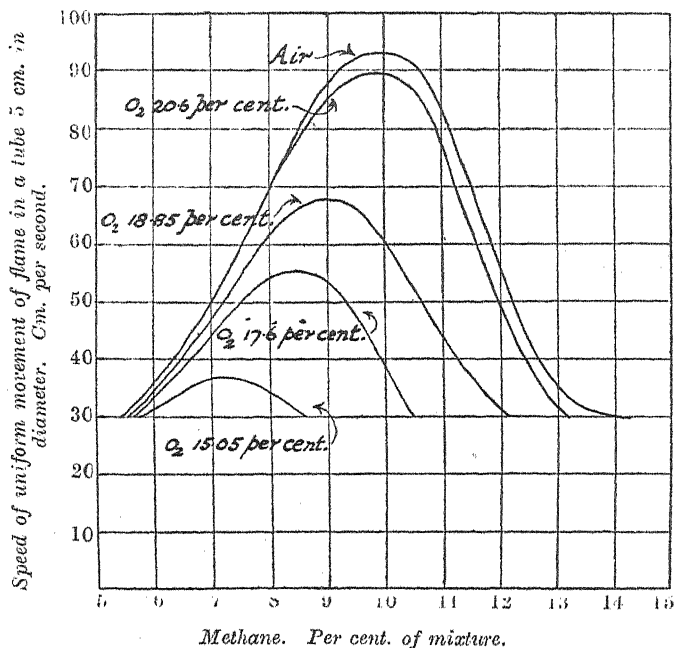
which the theoretical combustion-temperatures have been calculated.

The results are shown in Fig. 2, which, apart from the problem with which we are now concerned, is of interest in showing the effect of reducing the oxygen content of the air on its ability to support the combustion of methane. In the topmost curve the speeds of the flames are plotted against percentages of methane in atmospheric air *; the curve below was obtained with an "atmo-

* This curve, which is reproduced also in Fig. 3, is constructed from the figures given by Wheeler (T., 1914, **105**, 2606) after applying a correction

sphere " containing 20·60 per cent. of oxygen; then follow in succession curves obtained with atmospheres containing 18·85, 17·60, and 15·05 per cent. of oxygen respectively, the percentages of methane in each instance being percentages in the particular " atmosphere." (For example, the 7 per cent. methane mixture with the 15·05 per cent. oxygen " atmosphere " had the following composition: methane, 7·0; oxygen, 14·0; nitrogen, 79·0 per cent.)

It will be seen that the speeds of all the limit mixtures (in which a balance is struck between the heat generated on combustion and the heat required to start combustion) are the same. The calculated ratios $T - t / t - \theta$ for each limit mixture are, however, not the same, being greater by about 50 per cent. for the higher limit mixtures than for the lower.

Calculation of the theoretical combustion-temperatures of the mixtures is comparatively simple so long as they contain sufficient oxygen to burn the methane completely. When the oxygen is in defect it is necessary to take into account the mechanism of combustion of methane. This, in accordance with Bone's researches on the slow combustion of methane, and as Burgess and Wheeler found in their experiments with "limit" mixtures of methane, oxygen, and nitrogen (T., 1914, **105**, 2596), involves, as the reaction essential to the propagation of flame, the formation of carbon monoxide, hydrogen, and steam in equal volumes, according to the scheme:

$$\overset{(CH_2O)}{CH_4 + O_2} = CO + H_2 + H_2O.$$
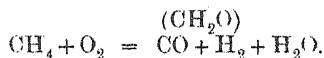
Following upon this reaction, the carbon monoxide and hydrogen are burned, practically completely to carbon dioxide and steam if the ratio O_2 / CH_4 is 2·0 or greater; or, if the ratio is less than 2·0, proportionally to the oxygen-concentration. Analyses of samples of the burnt gases taken during the propagation of flame, before their cooling enabled the "water-gas reaction" to come into play, showed that with the mixture containing the lowest ratio, O_2 / CH_4 (namely, 1·20 for the higher limit mixture with air), the proportion of the methane burned completely to carbon dioxide and steam was nearly 33 per cent.; whilst the proportion so burned increased regularly with the ratio O_2 / CH_4 to just over 99 per cent. for mixtures with a ratio 2·0.

that was found to be necessary by reason of the fact that the "standard" ½-seconds clock used for the determinations recorded 50 seconds per minute instead of 60. The speeds given in Wheeler's paper, although relatively correct (the paper dealt only with the relative speeds) are therefore too high by one-sixth.

The relative ignition-temperatures of the mixtures were determined in a manner which will be described in a subsequent paper. It was found that, over the range of mixtures covered by the experiments now described, there was a nearly regular increase in the ignition-temperature as the ratio O_2/CH_4 decreased. The relative ignition-temperatures can be regarded as ranging from 650° for a mixture containing 5·5 per cent. of methane in air to 700° for one containing 14·5 per cent.

When the ratios $T - t/t - \theta$ for all the mixtures comprised within the curves shown in Fig. 2 are calculated, it is found that Mallard and Le Chatelier's equation (2) holds very closely so long as the oxygen in the mixtures is in excess; that is to say, so long as it is possible for the combustion of the methane to be carried rapidly to completion. When the combustion is incomplete, however, the ratio $T - t/t - \theta$ is, in general, higher than the speed of the uniform movement of flame in the mixture requires. It becomes, as already stated, markedly high for the upper limit mixtures.

The natural inference to be drawn from this result is that there is an enhanced radiation loss through the walls of the tube during the propagation of flame in mixtures containing excess of methane, presumably because the process of combustion of such of the methane as burns is more protracted than when excess of oxygen is present, and the reacting molecules remain for a longer time in a condition of vibration such as to enable them to emit radiations. This presumed protraction of the process of combustion (of which a long, luminous tail behind the flame-front in mixtures containing excess of methane is perhaps evidence) would prevent the attainment of the calculated "combustion-temperature." It is, in fact, evident from these experiments that little meaning attaches to the usual calculations of combustion- or flame-temperatures, if only for the reason that the effect of the loss of energy by radiation, and the variations in that loss dependent on the duration of chemical change during combustion, are not taken into account.

The Influence of the Diameter of the Tube on the Speed of the Uniform Movement of Flame in Mixtures of Methane and Air.

According to Mallard and Le Chatelier, cooling of the hot gases by the walls of the tube does not appreciably affect the speed of the flame when the diameter is sufficiently great, for the following reasons: The quantity of heat withdrawn from the burning gases by the walls of the tube is proportional to the perimeter, $2\pi r$, of the tube; to the difference between the temperature of the gases and that of the tube, $T - \theta$; and to a coefficient of conductibility, k.

The mass of the burnt gases is proportional to r^2 and to the speed of propagation of the flame, v; so that, if Q be the heat of combustion and c the specific heat of the burnt gases,

$$Qr^2v = cr^2v(T-\theta) + kr(T-\theta),$$

whence $T = \theta + Q/(c + k/rv)$. The temperature T will not be materially affected when k/rv is negligible compared with c; that is to say, when r and v are sufficiently great.

For their experiments with mixtures of methane and air, Mallard and Le Chatelier used glass tubes 5 cm. in diameter, which they considered to be sufficiently large to overcome the effects of cooling by the walls even with the most slowly moving flames. This we believe to be correct, for there is not much difference in speed in tubes from 5 to 10 cm. in diameter, whereas when the diameter of the tube is only 2·5 cm., the speed is reduced by about one-third. Cooling by the walls thus interferes with the measurement of the true speed of the uniform movement of flame in mixtures of methane and air unless the diameter of the tube exceeds about 5 cm. When, however, the diameter is increased above 10 cm., the speed of the flames is affected by the coming into play of another factor, namely, convection.

The influence of convection currents is noticeable with the fastest moving flames in tubes 10 cm. in diameter, the visible effect being a turbulence of the flame-front. So far as can be judged by eye, the turbulence is essentially a swirling motion in a direction nearly normal to the direction of translation of the flame-front, which, as in tubes of smaller diameter, progresses at a uniform speed for about 150 cm. before backward and forward vibrations (the "vibratory movement") are set up. This swirling motion appears *ab initio*, and is due to rapid movement of the hot gases from below upwards by convection. In tubes of comparatively small diameter (5 to 9 cm.) this rapid movement is suppressed, although the shape of the flame-front shows that there is a definite movement of the hottest gases towards the upper part of the tube (see T., 1914, **105**, 2609).

We have determined the initial uniform speeds of the flames over the whole range of inflammable mixtures of methane and air in tubes 2·5, 5, 9, 30·5, and 96·5 cm. in diameter. The results are shown graphically in Fig. 3, in which the speeds of the flames are plotted against percentages of methane in air. If for any given mixture, say 10 per cent. methane, the speed of the flame is plotted against the diameter of the tube in which it travels, a curve such as those shown in Fig. 4 is obtained. From these curves it is clear that in tubes of less than 5 cm. diameter the speed of the flame is

retarded by the cooling effect of the walls.   In tubes of large diameter, however, from 10 cm. upwards, the speed of the flame is proportional to the diameter of the tube.

The "uniform movement" of flame as defined by Mallard and Le Chatelier (that is, "le mode de propagation par conductibilité") is thus a strictly limited phenomenon obtainable only in tubes

Fig. 3.

Methane.   Per cent. in air.
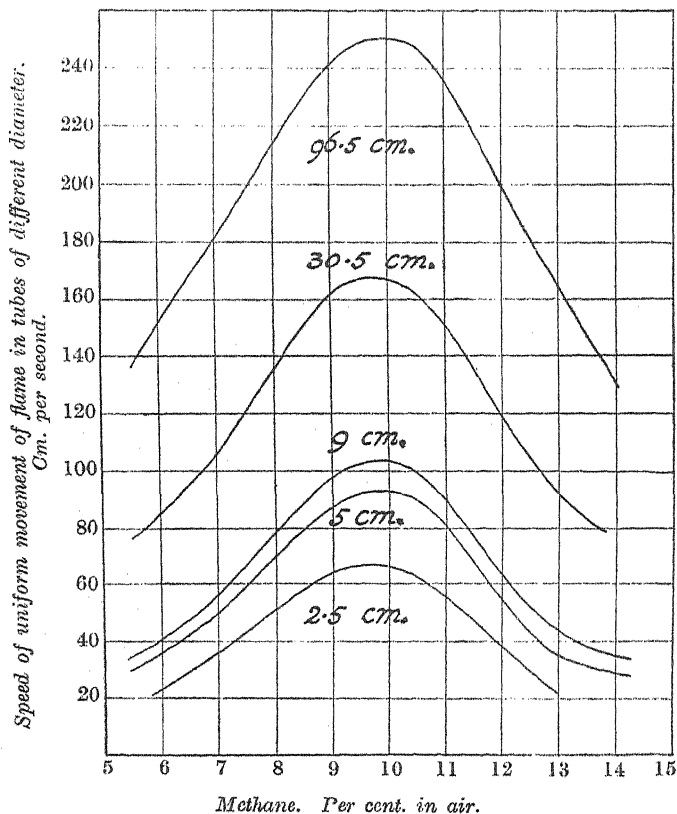
within a certain range of diameter, large enough to prevent appreciable cooling by the walls, but narrow enough to suppress the influence of convection currents.   The initial speed of flame in mixtures of methane and air is uniform also in tubes of large diameter—the flames travelled at a sensibly uniform speed over a distance of 10 metres in a tube 96·5 cm. in diameter and 44 metres long—but, as we have shown, this uniform movement does not

result from the normal transference of heat from layer to layer of the mixture by conduction.

When speaking of the uniform movement of flame in gaseous mixtures, it is necessary, therefore, if Mallard and Le Chatelier's definition be accepted, to specify the diameter of the tube in which the mixtures were contained. Alternatively, the initial slow uniform movement can be regarded simply as a particular phase in the propagation of flame that results when ignition is effected (in a quiescent mixture) at the open end of a straight, horizontal tube of any diameter closed at the other end; and not as resulting from a particular mode of heat transference.

FIG. 4.

Diameter of tube in cm.
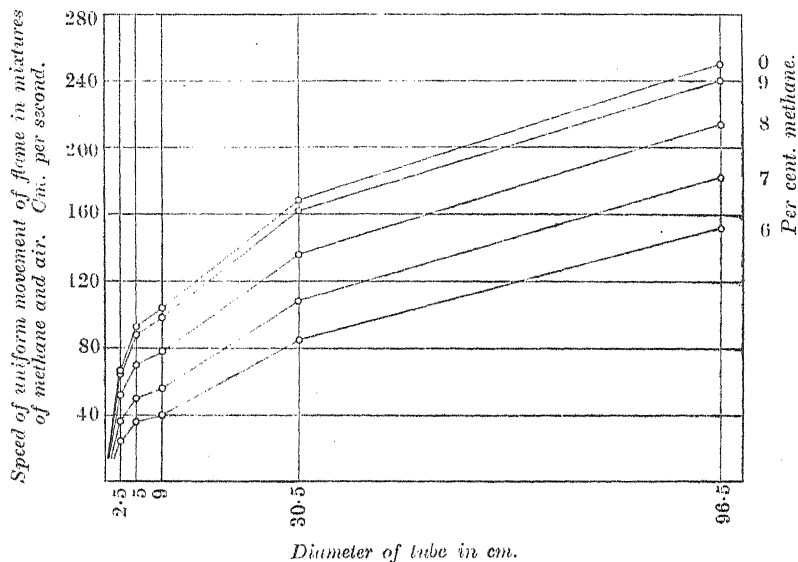
EXPERIMENTAL.

The method of recording the speed of the flames, and the general mode of procedure for the experiments in glass tubes, have been described by Wheeler (*loc. cit.*, p. 2610). The method was essentially that of registering on a chronograph the times at which fine screen-wires of copper (0·025 mm. in diameter), through which an electric current was passing, were fused as the flame reached them. We may add to the description already given the detail that the electric current passing through the screen-wires was sufficient to raise them nearly to red heat. This arrangement ensured the

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rapid melting of the wires as soon as the flame touched them, and therefore gave very uniform results; wires made from metals or alloys of low melting point, which could not be drawn so fine or of so uniform a diameter as copper, were found to be unsatisfactory.

For the experiments in the larger tubes (30·5 and 96·5 cm. in diameter respectively), which were of mild steel, the screen-wires were mounted on supports of brass wire reaching nearly to the horizontal axes of the tubes and fixed, through screwed-in plugs of vulcanite, 50 cm. apart along the length of each, the first screen-wire being 50 cm. from the point of ignition.

The tube of 30·5 cm. diameter was 15·24 metres long. It was filled with the required mixture, which had previously been prepared in a gas-holder of 42·48 cubic metres capacity, by displacement of air, six times the volume of the tube being taken for displacement. Samples of the mixture for analysis were taken from the gas-holder and from near the open end of the tube just before ignition. The analyses always closely agreed.

The tube of 96·5 cm. diameter was 44·25 metres long and was provided with a by-pass tube 15·24 cm. in diameter running its whole length, and fitted at either end with valves, which were closed during an experiment. A motor-driven fan was included in this by-pass connexion, and served to circulate the contents of both tube and by-pass when making the mixture of methane and air required for an experiment. The mixtures were made by passing into the tube a measured quantity of methane from a storage holder, displacing an equal quantity of air, and circulating the contents as aforesaid during two hours, the end of the tube at which the mixture was to be ignited being temporarily closed during this operation by a gas-tight cover of wood. Samples of the mixture for analysis were taken from both ends of the tube before each experiment; no appreciable difference was found between the compositions of samples of the mixture at either end of the tube.

For all the experiments, including those in the glass tubes, the methane used was from a blower of firedamp in South Wales, whence it was obtained compressed in cylinders. It contained no appreciable impurity other than between 2 and 2½ per cent. of nitrogen.

In the opening paragraphs of this paper we indicated some of the conditions necessary to ensure the obtaining of the uniform movement of flame. One of the essential conditions is that ignition should be effected *at or within* 3 *or* 4 *cm. of* the open end of

the tube.   This is particularly necessary with narrow tubes, other-
wise, if the point of ignition be some considerable distance within
the tube, flame travels in both directions from the point of ignition,
and the disturbance caused by the flame travelling towards the
open end affects the flame travelling towards the closed end.   The
result is that a vibratory motion is imparted at the outset to the
flame, and records of the speed of the flame travelling towards the
closed end show in consequence wide variations from one experi-
ment to another with the same mixture.

For example, the following records were made of the speed of
flame in a mixture of methane and air containing 10·00 per cent.
of methane.   A tube 5 cm. in diameter and 5·2 metres long was
used.   In one series of experiments, the point of ignition was 4 cm.
from the open end of the tube and in another it was 17 cm.   The
speeds were measured between two screen-wires 50 cm. apart, the
first screen being 40 cm. from the point of ignition.   Ignition was
by a secondary discharge across a 3 mm. spark-gap, using a
"4-inch" induction coil with a current of 2·5 amperes through the
primary circuit.

Speed of " Uniform Movement." Cm. per second.

	Point of ignition 4 cm. from open end.	Point of ignition 17 cm. from open end.
1	93·3	88·0
2	91·7	91·3
3	93·3	88·8
4	94·1	87·2
5	94·1	80·9
6	93·3	90·3
7	91·7	94·5
8	91·0	83·3
9	94·1	86·2
Mean	92·9	87·8
Variation	+1·2	+6·7
	−1·9	−6·9

Similarly, with a glass tube 2·5 cm. in diameter, when ignition
of a mixture of methane and air containing 10·25 per cent. of
methane was effected at a point 15 cm. from the open end, vibra-
tions were set up immediately in the flame travelling towards the
closed end, and wide variations were obtained in the records of
speeds, as follows:

Speed of "Uniform Movement." Cm. per second.

	Point of ignition 4 cm. from open end.	Point of ignition 15 cm. from open end.
1	65·5	59·1
2	65·5	50·0
3	66·2	52·5
4	65·5	57·0
Mean	65·7	54·6
Variation	+0·5	+4·5
	−0·2	−4·6

Apart from the wide variations in the recorded speeds when the point of ignition is too far within the tube, it will be seen that the mean of the results shows a slower speed than when the point of ignition is properly placed. The reason for this is that the flame that travels towards the open end acts as a drag on the flame travelling towards the closed end. In general, unless care be taken to avoid causing disturbance of the mixture at the moment of ignition, the records of speeds of flames obtained are of doubtful value.

Another matter that requires attention is the possibility of any additional impetus given to the flame by the source of heat used to cause ignition affecting the recorded speed. This can be avoided by allowing the flame to travel a distance of 30 or 40 cm. before reaching the first screen-wire (see T., 1914 ,**105**, 2610). When this precaution is taken, the intensity and size of the source of heat used to ignite the mixtures can be varied considerably without affecting the measurements of the speeds of the flames, as the following experiments illustrate.

A glass tube 2·5 cm. in diameter and 5 metres long was used, and the speed of the uniform movement of flame determined in a series of mixtures of methane and air. The mixtures were ignited by (i) secondary discharge sparks from an "8-inch" X-ray coil with a current of 5 amperes through the primary circuit; (ii) secondary discharge sparks from a "4-inch" coil with a current of 2·5 amperes through the primary circuit; and (iii) the flame of a taper. The point of ignition was 4 cm. from the open end of the tube when sparks were used; at the open end when the taper-flame was employed. The first screen-wire was 40 cm. from the open end of the tube.

Speed of " Uniform Movement." Cm. per second.

Methane. Per cent.	Ignition by " 8-inch " coil.	Ignition by " 4-inch " coil.	Ignition by taper.
7·10	37·0	37·3	36·6
7·80	47·0	47·7	47·5
8·05	51·0	52·5	52·1
8·60	57·3	58·0	58·7
9·10	64·6	64·0	64·4
9·50	66·6	68·3	66·6
9·95	66·2	67·8	65·5
10·25	65·5	65·5	66·2
10·55	61·0	61·8	61·5
11·60	46·7	47·5	47·9
12·25	35·0	35·1	35·0

It will be seen that for any of the mixtures the recorded speeds did not show any abnormal variations traceable to the means of of ignition employed.

XCIII.—*The Hydrolysis of Sodium Cyanide.*

By Frederick Palliser Worley and Vere Rochelle Browne.

In the extraction of gold by the cyanide process, the degree of hydrolysis of the sodium cyanide at the dilution employed is considerable, and any investigation of the chemical actions which occur in this process involves an accurate knowledge of the degree of hydrolysis of the cyanide in solutions of different concentrations. In an investigation of the chemical actions occurring in the dissolution of gold by solutions of sodium cyanide, the results of which will be published in a subsequent paper, it has been shown that the degree of hydrolysis of the cyanide is a most important factor in the rate of dissolution of the gold. The present paper deals with the degree of hydrolysis of sodium cyanide in solutions of widely different concentrations at temperatures from 0° to 30°.

The method employed is so simple that it would form a useful exercise for students of physical chemistry. It consists in comparing the concentrations of hydrogen cyanide vapour above solutions of sodium cyanide and of hydrocyanic acid by drawing the vapour through a solution containing 0·2 per cent. of picric acid and 2 per cent. of sodium carbonate. The intensity of the reddish-brown colour produced in the indicator solution varies

rapidly with the concentration of the hydrogen cyanide in the
vapour, and by comparing the colours produced when a stream
of air passes through a series of solutions of sodium cyanide of
one concentration alternating with solutions of hydrocyanic acid
of different concentrations, the strength of hydrogen cyanide solu-
tion can be found which has the same hydrogen cyanide vapour
pressure as the sodium cyanide solution.

EXPERIMENTAL.

The sodium cyanide was freshly prepared, and in order to
ascertain that no appreciable amount of free sodium hydroxide
was present, a sample was dissolved in water and titrated for
cyanide with a standard solution of silver nitrate, and for alkali
with standard hydrochloric acid, using methyl-orange as indicator.

The hydrocyanic acid was prepared immediately before use and

FIG. 1.
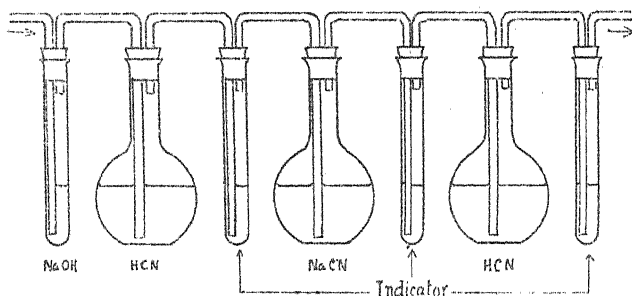
of the strength required by adding an equivalent amount of
hydrochloric acid to a solution of sodium cyanide.

In each experiment, two concentrations of hydrocyanic acid
were employed, one of which had a higher hydrogen cyanide
vapour pressure than the hydrocyanic acid solution and the other
a lower pressure. The solutions of cyanide and of hydrocyanic
acid were contained in 300 c.c. flasks and the indicator solutions
in test-tubes, 10 c.c. of the indicator solutions being used and
about 100 c.c. of the other solutions. The flasks and test-tubes
were arranged as in Fig. 1, a test-tube containing sodium hydr-
oxide solution being placed at the beginning in order to remove
carbon dioxide.

In a preliminary experiment, the difference in concentration
between the two acid solutions was considerable, thereby giving
an indication of the approximate strength required in order to

match the cyanide solution. In subsequent experiments, the difference in concentration could be made very much smaller, still allowing the intensity of colour produced by the cyanide to be intermediate between those produced by the two acid solutions or to coincide with one of them. Thus the concentration of hydrocyanic acid which had the same hydrogen cyanide pressure as the cyanide solution was determined within very narrow limits.

Air was drawn through the flasks at the rate of about one bubble per second.

At the higher temperatures, the apparatus was kept in a constant-temperature air-chamber electrically heated and electrically controlled, and at the lower temperatures in water at constant temperature or in melting ice. The temperatures employed were 0°, 5°, 10°, 15°, 20°, 25 and 30°.

Possible Sources of Error.—(1) By placing two indicator tubes together in series, it was found that the whole of the hydrogen cyanide was absorbed in the first, no perceptible change of colour being produced in the second. Thus one indicator tube after each flask was sufficient.

(2) The amount of hydrogen cyanide removed from the solution was found to be too small to affect the concentration or degree of hydrolysis of the solution. This was shown by measuring the degree of hydrolysis of the same solution of cyanide a second time, using fresh solutions of hydrocyanic acid, the result in the second case being the same as in the first.

(3) The possibility of error due to the slight pressure gradient in the series of flasks was avoided by placing the cyanide solution between the two acid solutions. By reversing the order of the two acid solutions, placing the stronger after the cyanide in one experiment and before it in another (the same strength of solution being used), no perceptible difference was observed, showing that the slight pressure gradient was negligible.

(4) In order to ascertain whether the effect of the non-hydrolysed sodium cyanide on the vapour pressure of the free hydrogen cyanide was of importance, experiments were carried out in which the hydrogen cyanide vapour pressure of hydrocyanic acid solutions containing sodium chloride was compared with that of solutions containing no salt. The presence of even large quantities of salt had no perceptible effect on the amount of hydrogen cyanide removed by the air, and it was consequently judged that the effect of the sodium cyanide was negligible.

Results.—From the equation expressing the hydrolysis of sodium cyanide,

$$NaCN + H_2O \rightleftharpoons NaOH + HCN,$$
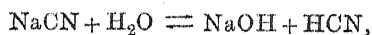
it is obvious that in the presence of a large excess of water the relationship between the concentrations of the various compounds should be expressed by the mass-action equation

$$\frac{[NaOH][HCN]}{[HCN]} = K.$$

and also that this relationship should hold in the presence of excess of either sodium hydroxide or of hydrocyanic acid. In the

FIG. 2.

Cube roots of concentrations.
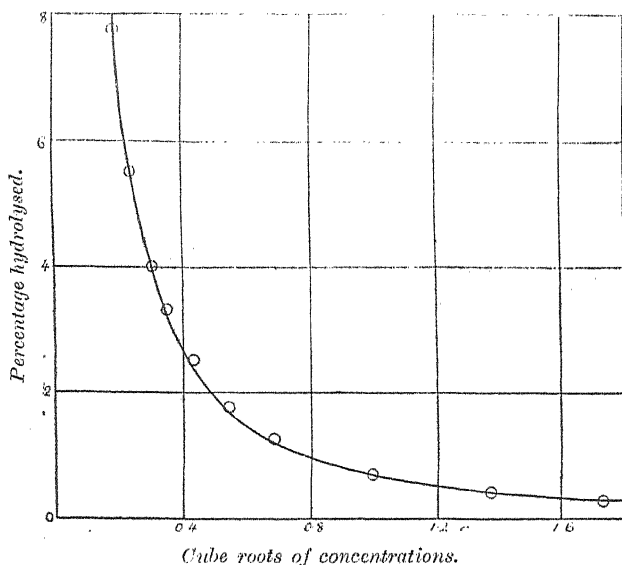
absence of excess of alkali or acid, if C is the concentration of the total sodium cyanide and P the percentage hydrolysed, then

$$\frac{P^2C}{100(100 - P)} K.$$

Experiments were carried out at 25° on the hydrolysis of sodium cyanide at a number of concentrations from 5·2 to 0·00725 gram-molecules per litre, and at a concentration of 0·0435 in the presence of different amounts of sodium hydroxide and of hydrochloric acid. In the latter case, it is obvious that an excess of hydro-cyanic acid equivalent to the hydrochloric acid was liberated. The results of these experiments are shown in tables I and II.

TABLE I.

Temperature, 25°.

Gram-mols. of NaCN per litre (C).	Percentage hydrolysed (P).	$K \times 10^4$.	P (calculated).
5·20	0·30	0·47	0·303
2·60	0·425	0·48	0·429
1·00	0·70	0·49	0·692
0·325	1·25	0·50	1·21
0·163	1·75	0·49	1·70
0·0813	2·5	0·50	2·40
0·0435	3·3	0·49	3·27
0·0290	4·0	0·48	3·99
0·0145	5·5	0·47	5·59
0·0073	7·75	0·47	7·82

Mean 0·484

TABLE II.

0·0435 *Gram-mols. of* NaCN *per litre.*

Gram-mols. of NaOH per gram-mol. of NaCN.	Percentage hydrolysed.	$K \times 10^4$.
1·00	0·11	0·48
0·50	0·225	0·50
0·25	0·45	0·50
0·01	2·8	0·47

Gram-mols. of HCl. per gram-mol. of NaCN.		
0·4	40·175	0·49
0·3	30·25	0·47
0·2	20·45	0·48
0·1	10·9	0·47

Mean 0·483

In the last column of table I is given the percentage of hydrolysis calculated from the mean value of the constant. It is obvious that there is no perceptible variation in K beyond that due to experimental error, and that there is remarkably little difference between the degree of hydrolysis found by experiment and that calculated from the mean value of K.

In Fig. 2, the curve expresses the calculated degrees of hydrolysis and the circles the experimental values, the abscissæ being the cube roots of the concentrations in order to produce a flatter curve. The effect of temperature on the value of the constant was found from experiments carried out at intervals of 5° from 0° to 30°. Fewer concentrations were used than at 25°, at some temperatures only one concentration being employed. The results are given in table III, the relationship between the tempera-

ture and the mean values of K being shown in the form of a curve in Fig. 3.

TABLE III.

Temperature.	C.	P.	$K \times 10^4$.	(Mean)
0°	0·550	0·50	0·14	0·135
—	0·0435	1·75	0·13	—
5	0·550	0·53	0·15	0·15
10	0·550	0·54	0·16	0·16
11	0·550	0·60	0·20	0·20
20	0·325	0·90	0·27	—
—	0·0435	2·5	0·28	
—	0·0145	4·25	0·27	0·27
—	0·0036	8·0	0·25	
25	Table I	—	—	0·484
30	0·325	1·5	0·74	—
—	0·0435	4·0	0·72	0·72
—	0·0145	6·75	0·71	—

FIG. 3.
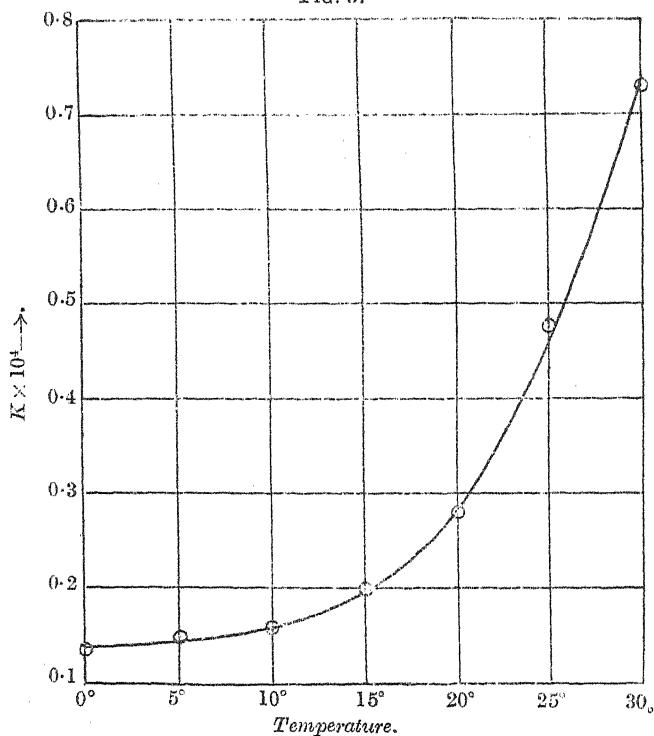
From these results, it is possible to calculate the degree of hydrolysis of solutions of sodium cyanide of concentrations up to $5 \cdot 2N$ at any temperature between 0° and 35°.

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XCIV.—*The Polysulphides of the Alkali Metals. Part III. The Solidifying Points of the Systems, Sodium Monosulphide–Sulphur, and Potassium Monosulphide–Sulphur.*

By John Smeath Thomas and Alexander Rule.

The formation of polysulphides by the action of sulphur on alcoholic solutions of the anhydrous hydrosulphides of sodium and potassium has previously been investigated and described by the authors (T., 1914, **105**, 177, 2819). By means of this reaction, it was found possible to prepare sodium tetrasulphide and potassium pentasulphide in the pure and anhydrous form, but it was observed that when attempts were made to utilise it for the preparation of other polysulphides of lower sulphur content, the above-mentioned compounds, contaminated to a greater or less extent with the corresponding hydrosulphides, were always obtained. This result is in general agreement with the work of Bloxam (T., 1900, **77**, 753).

By measuring the quantities of hydrogen sulphide evolved when known weights of the hydrosulphides of sodium and potassium were treated in boiling alcoholic solution with varying amounts of sulphur, the present authors (*loc. cit.*) have shown that the reaction between sulphur and the hydrosulphides of the alkali metals, in solution, tends to the formation of one polysulphide only; in the case of sodium the tetrasulphide, and in the case of potassium the pentasulphide.

The only polysulphide of sodium that Bloxam succeeded in preparing was the hydrated enneasulphide, to which he assigned the formula $Na_4S_9,14H_2O$. He described, however, a regular series of the potassium compounds, including an enneasulphide which he claimed to have isolated in the anhydrous state. The question of the existence of enneasulphides of the alkali metals will be discussed later. It may, however, be pointed out here that the present authors have failed to obtain any such compound either of sodium or potassium. Further, in view of the ease with which the polysulphides of these metals undergo hydrolysis, and taking into consideration the fact that Bloxam's preparations were carried out in aqueous solutions, the purity of the anhydrous polysulphides described by him seems open to question.

There is, however, considerable evidence of the existence, in aqueous solution, of a series of sodium polysulphides, from the disulphide to the hexasulphide, and possibly beyond, the work of

Küster and Heberlein on this point being specially important (*Zeitsch. anorg. Chem.*, 1905, **43**, 53; **44**, 431). These authors found that their results could only be explained satisfactorily by assuming that the solutions dealt with contained a number of anions of the type S'', S''_2, S''_3, etc., in equilibrium with each other.

The present investigation was undertaken with the view of resolving the present uncertainty as to the number and the relative stabilities of the solid polysulphides of sodium and potassium. Two main objects were kept in view. In the first place, it seemed desirable to decide whether higher polysulphides of these metals than those which have been described can exist in the solid state, and, secondly, the nature of the lower polysulphides and the question of the existence of intermediate compounds required to be settled. The last-mentioned point is of especial interest in view of Bloxam's conclusion (*loc. cit.*, and T., 1895, **67**, 277) that the enneasulphides of sodium, potassium, and ammonium can exist as stable compounds.

In order to account for these intermediate compounds, Bloxam suggested that the polysulphides of the alkali metals really consist of solid solutions of sulphur in fundamental compounds of the type R_4S_5, and that therefore the general formula assigned to them should be R_4S_x, where x may be any whole number greater than 5. In the case of rubidium and cæsium, Biltz and Wilke-Dörfurt (*Zeitsch. anorg. Chem.*, 1906, **48**, 297; **50**, 67; see also *Ber.*, 1905, **43**, 53), who thoroughly investigated the polysulphides of these metals by a thermo-analytical method, found no indication of the existence of the intermediate compounds required by this theory, and the present authors similarly have failed to confirm the existence of such compounds of sodium and potassium. On the other hand, positive evidence has been obtained in support of the simpler general formula R_2S_x.

EXPERIMENTAL.

The main portion of the experimental work described in this paper consisted of the determination of the freezing-point curves for the systems sodium monosulphide–sulphur and potassium monosulphide–sulphur. These curves were constructed in each case in two sections, the first consisting of that portion relating to mixtures in which the percentage of sulphur exceeded that required for the formation of potassium pentasulphide or sodium tetrasulphide, as the case might be, the second dealing with mixtures intermediate in composition between potassium pentasulphide or sodium tetrasulphide and the corresponding disulphide.

In a second series of experiments, the higher polysulphides were heated in a steady stream of hydrogen, and the rate of desulphurisation was determined by weighing at regular intervals. During each period of heating, the temperature was kept as nearly constant as possible, but it was regularly increased for successive periods.

Finally, in order to decide between the simpler formula R_2S_x and the double formula advocated by Bloxam, molecular weight determinations were carried out in the cases of those compounds which could be obtained in the pure state. For this, the ebullioscopic method was employed, alcohol being the solvent.

The hygroscopic nature of the substances dealt with made it necessary carefully to exclude moisture at every stage, whilst, owing to the ease with which they oxidise, all solidifying-point measurements had to be made in a stream of pure dry nitrogen. Frequently mixtures were obtained, especially when the composition was not that of a compound, which supercooled to a remarkable extent, and it was sometimes possible to keep these mixtures in the supercooled condition for several days at the ordinary temperature. The crystallisation of these supercooled mixtures was usually accompanied by considerable increase in volume, and it often took place so rapidly that the crucible containing the mixture was shattered.

Preliminary experiments showed that at temperatures above 400° the fused substances attacked glass to an appreciable extent, the disulphides being more active in this respect than the tetra- or the penta-sulphides. Except at much higher temperatures, they are, however, all without marked action on glazed porcelain, and vessels of this material were therefore used to contain them.

For the determination of solidifying points below 300°, the apparatus used was very simple. It consisted of a weighed crucible of glazed porcelain in which the weighed substance, from 15 to 20 grams in amount, was placed. The crucible was then lowered to the bottom of a hard glass tube, about 30 cm. long, the lower end of which was sealed. This tube was clamped in a vertical position, and its upper end was fitted with a rubber stopper through which passed a thermometer, a porcelain stirrer, the exact weight of each having previously been determined, and two gas-delivery tubes. One of these tubes just passed through the stopper, whilst the other reached almost to the bottom of the apparatus. By their means, the air was displaced by dry nitrogen. The mixtures were fused by heating the apparatus in an oil-bath, and a similar bath was used to maintain a constant external temperature during solidification.

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In consequence of the high melting points observed in the region of the disulphides, it became necessary to employ a form of apparatus more suited to their measurement than the one just described. An electrically heated arrangement was finally adopted.

This consisted of an internally glazed porcelain tube of approximately 3·5 cm. in diameter and 50 cm. long, clamped in an upright position. A portion of this tube was wound with nickel-chromium wire; current from the lighting circuit was used, and loss of heat by radiation, and oxidation of the wire were prevented by surrounding the wound section of the tube with a thick layer of kieselguhr.

It was found that temperatures up to 800° could easily be attained, and that when equilibrium conditions had been established, any desired temperature could be maintained, with very slight variation, over considerable periods of time. The pyrometer consisted of a platinum–platinum-iridium thermo-element in conjunction with a millivoltmeter, which was carefully calibrated. The hot junction was protected from the action of the fused substances by enclosing it in a very thin-walled porcelain tube. For the reasons previously mentioned, silica could not be used for this purpose, and it was found inadvisable to employ platinum.*

The lower portion of the furnace tube was packed with kieselguhr, through which a silica tube of small bore passed. On the kieselguhr, the crucible was supported so as to rest in that region of the furnace where the temperature was most uniform. It was placed in position and removed by means of a stout platinum wire looped round it. A rubber stopper pierced with four holes closed the upper end of the tube. Through these holes passed the pyrometer tube, the stirrer, the platinum wire referred to, and, lastly, a delivery tube which, used in conjunction with the silica tube at the lower end, allowed of the displacement of the air by dry hydrogen or nitrogen.

The pure potassium pentasulphide and the di- and tetra-sulphides of sodium used in these experiments were prepared by the methods described in earlier papers of this series (*loc. cit.*). After preparation, they were kept in a vacuum desiccator over phosphoric oxide.

It has previously been pointed out that potassium disulphide

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[1] In some early experiments the hot junction was protected by a platinum tube, but at the close of the series the metal was found to be considerably lighter in weight. On dissolving the fusion a brown, insoluble powder was obtained, which from a partial examination appeared to be platinum mono-sulphide. The quantity obtained, however, was insufficient to allow of a complete examination.

cannot be obtained by a method analogous to that employed for the preparation of the corresponding sodium compound, since the reduction of the pentasulphide by metallic potassium yields a polysulphide mixture consisting mainly of the trisulphide, but containing a considerable amount of other substances, the removal of which is very difficult. In their work on the polysulphides of rubidium and cæsium, Biltz and Wilke-Dörfurt (*loc. cit.*) obtained mixtures of low sulphur content by strongly heating the pentasulphides in a stream of hydrogen. It was decided to use this method for the preparation of potassium disulphide. For purposes of comparison, sodium disulphide was also prepared in this way, and a series of solidifying-point determinations was made with material so prepared as the starting point. The results obtained in this series were found to agree very closely with those recorded in experiments in which sodium disulphide prepared by reduction formed the starting material.

The sulphur used was twice recrystallised from carbon disulphide and then heated for several hours at 100° in order to remove the last traces of solvent. This substance was also preserved in a desiccator over phosphoric oxide.

The Desulphurisation of Sodium Tetrasulphide and Potassium Pentasulphide.

The primary object of these experiments, as has already been mentioned, was the preparation of the materials necessary for the construction of the complete solidifying-point diagrams of the systems under consideration. The removal of sulphur from the easily prepared higher polysulphides was effected by heating them in a steady stream of hydrogen. At half-hourly intervals, the heating was interrupted, and, after cooling, the amount of sulphur lost by the substance was determined by weighing. During each period of heating, the temperature was kept as nearly constant as possible, and its value was 25° higher for each period than for the one immediately preceding. The variations in the rate of removal of sulphur yielded valuable information with regard to the existence of lower compounds, and especially as to their relative stabilities.

The heatings were carried out in a slightly modified form of the electrically heated furnace already described. A porcelain crucible of known weight and containing the weighed substance was introduced into the furnace tube and the stream of pure, dry hydrogen started. The gas was prepared by the electrolysis of a solution of barium hydroxide, using a current of constant strength, thus

avoiding variations in its rate of flow. During the time that the
temperature of the furnace was being adjusted to the constant
value desired, the crucible was drawn into the cool upper portion
of the tube, and on the expiration of each heating period the sub-
stance was cooled quickly in the same way.

Fig. 1.

Loss in weight per 100 grams of sodium tetrasulphide.
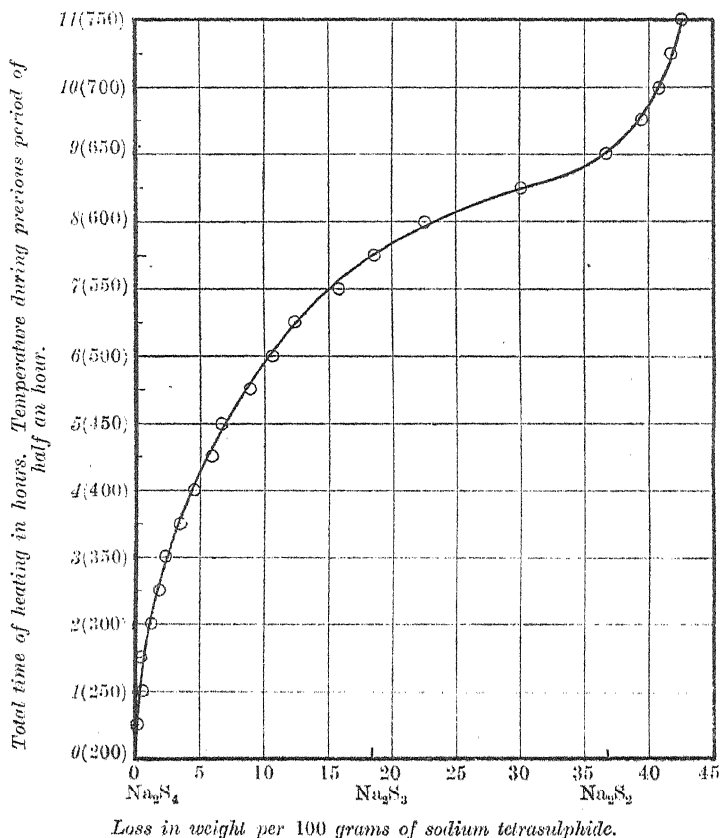
The weight of sodium tetrasulphide taken was 15·673 grams, and
an analysis of the substance gave the following figures:

0·5657 gave 0·4624 Na_2SO_4. $Na = 26·47$.
0·2464   ,,   1·3178 $BaSO_4$. $S = 73·47$.
   Na_2S_4 requires $Na = 26·44$; $S = 73·56$ per cent.

The results obtained are represented graphically in Fig. 1, in
which the loss in weight per 100 grams of sodium tetrasulphide is

plotted against the total time of heating. The temperature maintained during the previous half-hour is shown, and points are given at which, from the loss of weight, the fused material should have the composition of the mono-, di-, and tri-sulphides.

As will be seen from the curve, the tetrasulphide undergoes considerable decomposition below 300°, and from this point the velocity with which the sulphur is removed increases regularly as the temperature rises until the composition of the fusion approaches that of the disulphide, the temperature by this time having risen to between 625° and 650°. Before the loss reaches that calculated for the disulphide, however, the direction of the curve changes markedly, and the removal of sulphur proceeds much more slowly. This retardation is indeed so marked as to render the preparation of the monosulphide by this method, at the temperatures attainable in the apparatus described, practically impossible.

The values given on the curve are, of course, only relative, since the rate of loss of sulphur must obviously depend on the surface area exposed by the fused substance and also on the rate of flow of the hydrogen stream. They do, however, indicate the existence of a disulphide, the stability of which towards heat far exceeds that of the higher compounds.

The total loss of weight in the course of the experiment was 6·575 grams, and the composition of the product should therefore be $Na = 45·43$; $S = 54·57$ per cent.

Analysis of the product gave the following results, which agree well with the composition calculated from the loss in weight:

0·4846 gave 0·6795 Na_2SO_4. $Na = 45·40$.
0·3725 ,, 1·4810 $BaSO_4$. $S = 54·62$.
Na_2S_2 requires $Na = 41·76$; $S = 58·24$ per cent.

From the excellent agreement between the composition of the product as determined analytically and that calculated from the loss in weight, it is clear that the sodium polysulphides do not volatilise to any appreciable extent when they are heated at temperatures within the limits mentioned, and this was found to be equally true in the case of the potassium compounds. Biltz and Wilke-Dörfurt (*loc. cit.*) found, however, that when the disulphides of rubidium and cæsium were prepared by this method, volatilisation invariably occurred, and to a greater extent in the case of the cæsium compounds than in the case of those of rubidium. It would seem, therefore, that the polysulphides of the alkali metals, like the halogen salts, show an increasing tendency to volatilise with rise in the atomic weights of the metals from which they are derived.

Turning to the preparation of potassium disulphide, the weight of the pentasulphide taken was 17·853 grams. The purity of the salts was established by analysis, in which the following results were obtained:

0·3587 gave 0·2816 K_2SO_4.   K = 32·76.
0·2752   ,,   1·3429 $BaSO_4$.   S = 67·09.
        K_2S_5 requires K = 32·78; S = 67·22 per cent.

FIG. 2.

Loss in weight per 100 *grams of potassium pentasulphate.*
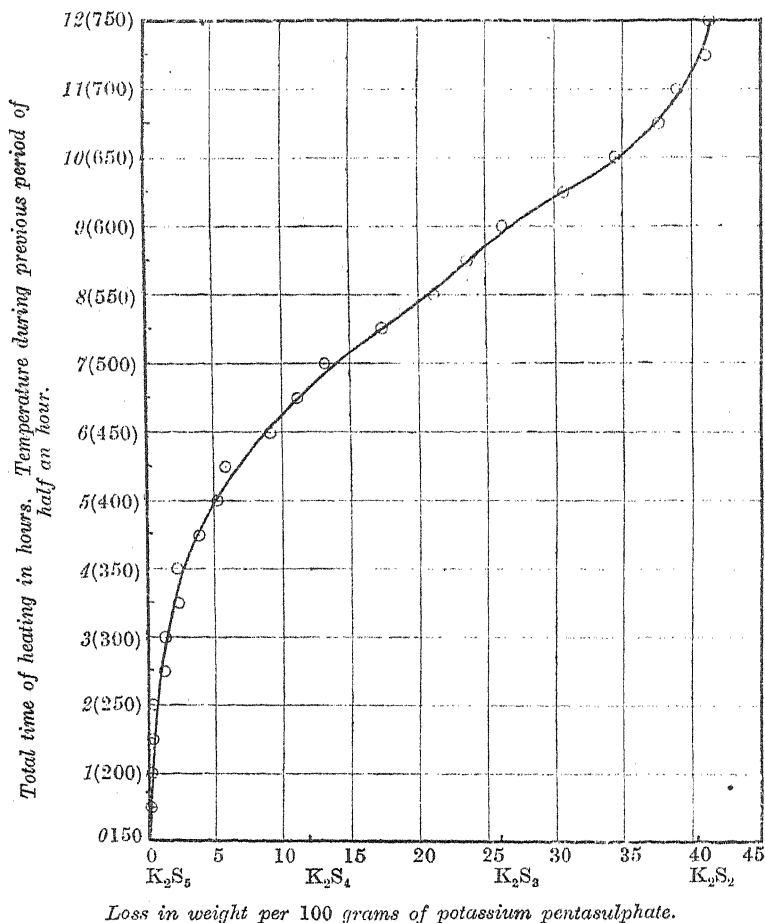
The removal of sulphur was effected and controlled in the manner already described, and the results obtained are shown graphically in Fig. 2.

Whereas sodium tetrasulphide decomposes slightly at its melting point, 274°, and loss of sulphur is appreciable at 300°, potassium pentasulphide appears to be more stable at its melting point, although in this case also appreciable loss of sulphur occurs at 300°.

As in the case of the sodium compound, the rate of removal of sulphur increases regularly as the temperature is raised, but the curve appears to indicate a slight retardation when the composition of the fusion approximates to that of the trisulphide, thus furnishing evidence of the existence of that compound as a substance the sulphur pressure of which remains constant betwen definite temperature limits.   In the case of potassium, also, the great stability of the disulphide may be deduced from the marked change in the direction of the curve when the composition of the fusion approaches that of that compound.   Even at 750° the further removal of sulphur takes place very slowly indeed.

The final product of the experiment, after cooling, was analysed, and gave the following figures:

0·3935 gave 0·4838 K_2SO_4. $K = 55·17$.

0·4017   ,,   1·3008 $BaSO_4$. $S = 44·49$.

K_2S_2 requires $K = 54·94$; $S = 45·06$ per cent.

The total loss in weight was 7·306 grams, and from this, assuming that no volatilisation of the sulphides had taken place, the composition of the product should have been $K = 55·46$; $S = 44·54$ per cent.

It is evident that sulphur had been removed in excess of the amount required for the formation of potassium disulphide.   The agreement between the values obtained and those calculated from the loss in weight is not so good as in the previous experiment, but the divergence lies within the limits of reasonable experimental error.   Since on examination of the furnace tube no trace of sublimed sulphide, such as Biltz and Wilke-Dörfurt describe in the cases of the rubidium and cæsium compounds, was found, it was concluded that, as in the case of the sodium compounds, no appreciable volatilisation had occurred.

Both potassium pentasulphide and sodium tetrasulphide fuse to deep red, almost black liquids, and this is also true of the various products obtained from them by the removal of sulphur.   On solidification, the penta- and tetra-sulphides crystallise quickly with very little supercooling, and the disulphides also crystallise quite readily, although supercooling is more marked in their case.

Between the di- and the tetra-sulphides, however, and especially in the neighbourhood of the trisulphides, red, glass-like substances were always obtained.   In these cases, inoculation often failed to

promote crystallisation, and the amorphous substances thus obtained could be kept for considerable periods at the temperature of the laboratory. Crystallisation usually took place with great rapidity when the temperature was raised, and, owing to its being accompanied by considerable increase of volume, shattering of the containing vessel commonly resulted. After crystallisation, the mass usually remained transparent and red, but presented the appearance of fracture in all directions.   When the substances after crystallisation were allowed to remain, the crystalline form apparently changed, and the mass became opaque and pale yellow, the depth of the colour depending on the percentage of sulphur in the substance.   In all cases the products were soluble in water, forming clear, yellow solutions, which, however, rapidly became cloudy owing to oxidation. The solutions of the disulphides were only faintly coloured, but increase in the sulphur content was in each case accompanied by a progressive increase in the intensity of the coloration.

The System, Sodium Monosulphide–Sulphur.

The apparatus employed in the investigation of this system has already been described. Every experiment was carried out in a stream of nitrogen which had been passed over red-hot copper and then over phosphoric oxide.

During the cooling of the mixtures, the temperature was read every fifteen seconds. The accuracy of the measurements depended not only on the exactness of the temperature readings, which in the case of the thermometer could be trusted to $0.2°$, and in that of the pyrometer to $1—1.5°$, but also on the general tendency of the curve and the ease with which crystallisation could be induced. Thus the error in the neighbourhood of the disulphide, where the curve is steep, is probably far greater than in the regions where the curve is comparatively flat.   Similarly, higher accuracy is attainable in the case of those mixtures which solidify sharply without supercooling than in the case of those in which the tendency to supercooling is very great, and crystallisation, even in the most favourable circumstances, only proceeds slowly. In these cases, the error in single determinations may be relatively great.

The results obtained in the analysis of the original material used for the construction of the section of the diagram lying between the disulphide and the tetrasulphide have already been given. On analysis, the tetrasulphide employed as starting material for the mapping out of the remaining portion of the curve gave the following figures:

0·4931 gave 0·4019 Na_2SO_4.   Na = 26·39.

0·2785   ,,   1·4904 $BaSO_4$.   S = 73·52.

Na_2S_4 requires Na = 26·44; S = 73·56 per cent.

At the commencement of each series of experiments, the substance, the crucible containing it, and also the thermometer and stirrer employed, were weighed. After each solidifying-point determination, the fusion was allowed to cool in an atmosphere of nitrogen, and, when cold, after removing the volatilised sulphur, the substance, etc., were re-weighed. The increase in weight gave

FIG. 3.
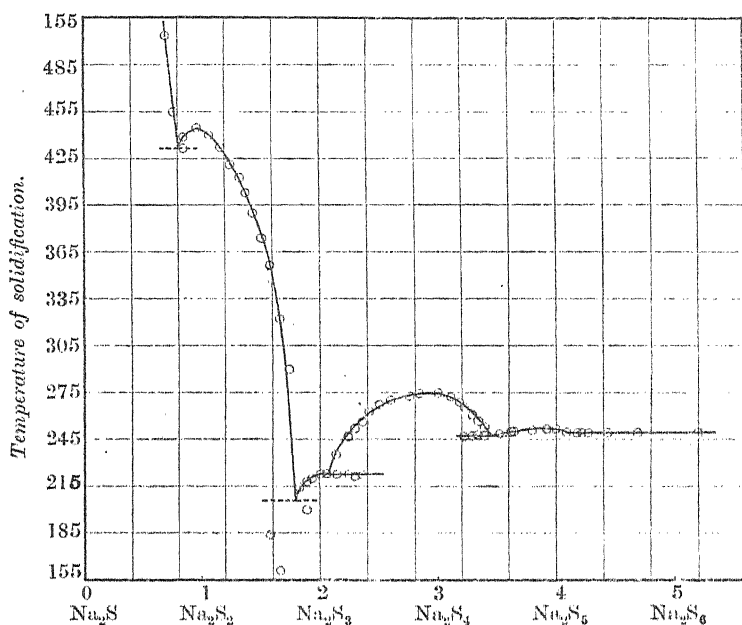
Composition : Atoms of sulphur per molecule of sodium monosulphide.

the amount of sulphur actually added, and from this the percentage composition of each fusion was calculated.

As a check on the compositions determined in this way, the final mixture obtained in each series of measurements was analysed. In every case the analytical results agreed well with the percentage compositions calculated from the total increase in weight.

In table I, the experimental results obtained for the different mixtures investigated are given, and they are also graphically represented in Fig. 3. In this diagram, the solidifying points of

TABLE I.

Percentage of Sulphur in mixture.	Number of gram-atoms of sulphur per gram-molecule of Na_2S.	Solidifying point.	Solidifying point of eutectics.	Remarks.
54·57	0·723	504	—	
55·25	0·771	455	—	
56·39	0·855	439	432	
57·91	0·970	445	—	
59·04	1·067	440	—	
60·18	1·168	432·5	—	Eutectic point doubtful. Approximate m. p., Na_2S_2.
61·08	1·252	421·5	—	
61·91	1·330	413	—	
62·38	1·380	403·5	—	
62·92	1·437	390	—	
63·63	1·513	374	—	
64·25	1·580	356·5	184	
64·95	1·662	322	160	
65·74	1·752	290	?	Probably m. p. eutectic $=206$.
66·10	1·800	206	206	This point is taken from the curve.
66·32	1·829	214·5	?	The eutectic solidified amorphous and this accounts for the wide difference in the values observed.
66·74	1·883	218	200	
67·14	1·935	220	—	
67·69	2·010	223	—	m.p., Na_2S_3, taken as 223·5°.
68·05	2·060	223·5	—	
68·61	2·140	235·5	223	
69·29	2·241	246	223	Mean solidifying point of eutectic $=222·6°$.
69·67	2·301	252	221·9	
70·13	2·364	256	222·5	
70·42	2·421	263	—	
71·25	2·550	267·5	—	
72·35	2·760	273	—	
73·56	3·000	275	—	Solidifying point of Na_2S_4.
74·15	3·114	272·5	—	
74·45	3·180	269	—	
74·62	3·217	266	247	
74·96	3·294	260·5	247·5	Mean solidifying point of eutectic $=247·6°$.
75·17	3·342	257·4	248	
75·38	3·392	253·5	247·8	
75·72	3·522	248·7	—	
76·29	3·615	250	—	
76·37	3·636	250	—	
76·97	3·794	251	—	
77·43	3·921	251·8	—	
77·71	4·001	251·7	—	Solidifying point of Na_2S_5.
78·03	4·094	250	—	
78·31	4·179	249·5	—	
78·41	4·209	249·7	—	Saturated solutions of sulphur in Na_2S_5 with m. p. 249·6°. The other layer was sulphur with solidifying point 118°.
78·63	4·278	249·7	—	
79·15	4·445	249·5	—	
80·15	4·792	249·6	—	
81·18	5·200	249·4	—	

These points were determined pyrometrically.

the mixtures used are plotted against their compositions, the latter being expressed as the number of gram-atoms of sulphur added per gram-molecule of sodium monosulphide.

As will be seen by reference to the curve, the system contains two well-defined eutectics, the first of which lies between the tri-sulphide and the tetrasulphide, contains 68·15 per cent. of sulphur, and melts at 222·6°, whilst the second lies between the tetra- and penta-sulphide. The melting point of this second eutectic is 247·6°, and it contains 75·48 per cent. of sulphur. In addition to these, there can be no doubt from the general tendency of the curve that eutectics also exist between the di- and tri-sulphides, and also between the monosulphide and the disulphide. Owing to undercooling, the melting point of the di-tri eutectic could not be determined accurately, but it is in the neighbourhood of 206°, and the mixture contains approximately 65 per cent. of sulphur.

For the definition of the monosulphide-disulphide eutectic, only one observation was obtained, and this was made pyrometrically. The halt, which was fairly distinct, occurred at a temperature of 432°. Although the existence, and especially the exact solidify-ing point, of this eutectic mixture cannot be considered to be determined by such a single measurement, it should be pointed out that the observation is in agreement with the general direc-tion of the curve, so that, on the whole, the conclusion is justified that the mono-di eutectic does exist, and that its solidifying point is probably in the neighbourhood of 430°. It contains approxim-ately 55·8 per cent. of sulphur.

The solidifying point of the monosulphide has not been deter-mined, since a sufficiently high temperature could not be obtained in the apparatus employed. It would seem probable, however, from the direction of that portion of the curve which lies between the monosulphide and the mono-di eutectic, as defined by the two points actually observed, that the melting point of the mono-sulphide must exceed 800°.

Turning to the maxima exhibited by the diagram, the first maximum occurs when the composition of the mixture corresponds with the disulphide, the temperature being 445°. From the fact that on either side of this point the curves fall away very steeply, it follows that the disulphide is quite stable towards heat at its melting point.

From the disulphide, the solidifying points of the mixtures fall nearly 250° until the di-tri eutectic is reached, from which point they again rise, but much less rapidly. In the case of the tri-sulphide, a definite maximum is not shown, but the existence of this compound is established, first, by the pronounced break which

is observed in the curve when the mixture has the composition of the trisulphide, and, secondly, by the presence of both di-tri and tri-tetra eutectics.

The absence of a definite maximum is evidence of the unstable character of the trisulphide, which must decompose at a temperature below its melting point.

From the break indicating the existence of the trisulphide, the curve again rises to a maximum at 275°, at which point the fusion has the composition of the tetrasulphide. Thus the existence of this compound as a substance stable at its melting point is established.

The behaviour of mixtures containing a higher percentage of sulphur than the tetrasulphide is interesting. As the sulphur content is increased, the solidifying points become lower until the tetra-penta eutectic melting at 247·6° is reached. From this point the curve appears to be almost horizontal, but on closer inspection a very slight rise can be seen which reaches a maximum at 251·8°, the rise therefore being only 4·2°. At this maximum point, the substance has a composition practically identical with that of the pentasulphide.

Kremann (*Monatsh.*, 1904, **25**, 1311) has shown that in the case of additive compounds, dissociation must theoretically result in the flattening of the maximum, and that this flattening must be the greater the greater the extent to which dissociation takes place. He has investigated cases, for example, trinitrobenzene-naphthalene, in which the solidifying points of both eutectics and that of the compound only differ by one or two degrees. It would appear that in the case of sodium pentasulphide, the fused substance is so strongly dissociated that the dissociation products are able to lower the maximum to a point very little above the tetra-penta eutectic on the one hand, and the solidifying point of the saturated solution of sulphur in sodium monosulphide on the other. Abegg and Hamburger (*Zeitsch. anorg. Chem.*, 1906, **50**, 435) have recorded a similar observation in the case of the poly-iodides of potassium, and their results have been confirmed by Kremann (*Monatsh.*, 1912, **33**, 1081). In this case, the difference between the maximum and the eutectic temperatures was found to be 3·7°.

The results obtained by the authors in their present investigation lead to the conclusion that the pentasulphide is the highest polysulphide obtainable by fusing together sodium monosulphide and sulphur, for immediately beyond the pentasulphide maximum the curve becomes horizontal, indicating the formation of a saturated solution of sulphur in the latter compound. The melt-

ing point of the saturated solution is 249·6°, and several points were obtained differing from this value by only 0·1—0·2°, although the sulphur content was varied considerably.

In order to make quite certain that this horizontal line really represented the formation of a saturated solution, the solidifying point of a mixture of equal amounts of sodium tetrasulphide and sulphur was determined. After the fused mixture had been thoroughly stirred, it separated into two layers, the lower of which, the saturated solution, solidified at 249·4°, whilst the upper layer of sulphur remained liquid until the temperature had fallen to 118°, when it solidified to a pale yellow mass. From the appearance of the sulphur so obtained, and also from its solidifying point, it would seem that the sodium polysulphides do not dissolve in molten sulphur to any appreciable extent.

No evidence whatever is furnished by the results obtained in this investigation of the existence of intermediate compounds, such as the enneasulphide. If intermediate compounds exist at all, they can only do so at low temperatures.

The System, Potassium Monosulphide–Sulphur.

The methods and apparatus employed in the investigation of this system were exactly similar to those already described when dealing with the sodium series.

As starting materials, the pure pentasulphide was used in one case, and mixtures obtained by expelling sulphur from the pentasulphide by heating it in a stream of hydrogen were employed in other series. Analyses of the pentasulphide and of a mixture containing less sulphur than the disulphide have already been given. In addition to these, a third material was employed, which on analysis gave the following results:

0·4971 gave 0·4639 K_2SO_4. $K = 41.88$.
0·2333   „   0·9856 $BaSO_4$. $S = 58.04$.

These figures agree well with the composition calculated from the loss in weight, and the substance therefore approximates to the trisulphide.

At the end of each series of determinations the final product was analysed. In every case the figures obtained were found to be in good agreement with the composition calculated from the weight of sulphur added in the course of the series.

The results obtained are given in table II, and in Fig. 4 they are represented graphically.

TABLE II.

Percentage of Sulphur in mixture.	Number of gram-atoms of sulphur per gram-molecule of K₂S.	Solidifying point.	Solidifying point, of eutectics.	Remarks.
44·55	0·959	467·5	—	
45·56	1·041	468	—	
46·89	1·145	464·5	—	
48·09	1·259	452·5	—	These points were deter-
49·18	1·360	433	—	mined pyro-
50·63	1·501	390·5	254	metrically.
51·97	1·638	360	249	Di-tri eutectic.
53·02	1·752	311	249	Mean m. p. = 250·9.
54·32	1·900	251·5	251·5	
55·51	2·042	251·6	—	
57·06	2·240	238	—	
57·78	2·342	217·4	—	
58·93	2·499	189	—	
59·62	2·600	160·5	—	
60·15	2·691	101 ?	101 ?	Amorphous. Probably tri-tetra eutectic.
60·55	2·743	130·7	—	
60·95	2·807	141·6	—	
62·02	2·983	145·5	—	
62·38	3·043	152	144	
62·72	3·102	166	142·5	Tetra-penta eutectic.
63·70	3·279	178·2	145	Mean m. p. = 143·4.
64·58	3·445	192	142	
65·74	3·680	201·9	—	
66·79	3·905	204·3	—	
67·22	4·001	206·5	—	
67·99	4·179	204·2	—	
68·73	4·360	200	—	
69·21	4·480	196·7	183	
69·59	4·580	192·2	183·7	
69·81	4·637	190	183·1	Penta-hexa eutectic.
70·26	4·709	187	182·4	Mean m. p. = 182·9°.
70·57	4·847	185·2	182·2	
70·86	4·930	188·6	—	
71·21	5·031	188·9	—	
71·56	5·135	188	—	Saturated solution of sulphur in
72·26	5·352	188·1	—	K₂S₆, m. p. = 188·1.
74·11	5·981	187·9	—	The sulphur layer solidified at 117·5°.
76·42	6·902	188·3	—	

An examination of the diagram renders quite clear the existence of three well-defined eutectic horizontal lines which lie between the di- and tri-sulphides, the tetra- and penta-sulphides, and the penta- and hexa-sulphides respectively. The eutectic mixtures corresponding with these horizontal lines have the following compositions and melting points:

Di-tri eutectic, S=54·32 per cent., m. p. 250·9°.
Tetra-penta eutectic, S=62·31 per cent., m. p. 143·4°.
Penta-hexa eutectic, S=70·39 per cent., m. p. 182·9°.

Owing to the difficulty of obtaining the necessary material and the previously mentioned limitation of the apparatus employed, the region between the mono- and di-sulphides has not been investigated.

Between the trisulphide and the tetrasulphide a region was encountered in which the tendency of the fusions to form highly supercooled, amorphous masses was very marked, and here no trust-

FIG. 4.
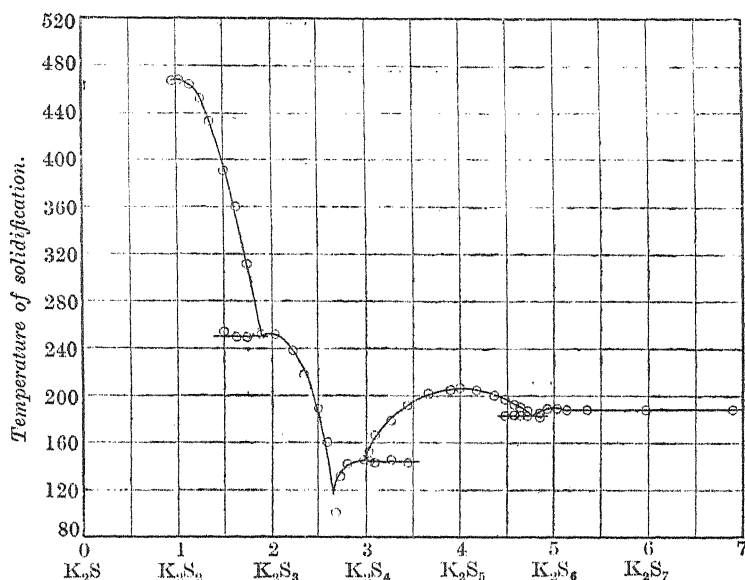
Composition : *Atoms of sulphur per molecule of potassium monosulphide.*

worthy transition points could be obtained. It seems probable that the amorphous substance referred to in the table really consists of the tri-tetra eutectic mixture.

The curve exhibits five maxima, of which those corresponding with the di-, tri-, and penta-sulphides are quite distinct. They occur at temperatures of 470°, 252°, and 206·5° respectively. The compounds mentioned, therefore, can exist as stable substances at their melting points.

Of the two remaining maxima, that which indicates the existence of the hexasulphide, and is found at 189°, is flattened in the

same way as the previously discussed sodium pentasulphide maximum, being but 1° higher than the saturated solution line on the one hand and 6° above the penta-hexa eutectic on the other. Potassium hexasulphide is therefore very considerably dissociated at its melting point.

In the case of the tetrasulphide, the curve shows no definite maximum, but the existence of this compound, the least stable towards heat of the polysulphides of potassium, is indicated by the decided break observed in the curve at the point where the composition of the fusion corresponds with that of this compound. The temperature at which this break occurs is 145·5°.

At 188°, when the mixture contains 71·5 per cent. of sulphur, the curve becomes horizontal, and the addition of comparatively large amounts of sulphur does not affect the solidifying point. When a sufficiently large amount of sulphur is added separation into two layers can be observed, the one consisting of a saturated solution of sulphur in the hexasulphide, solidifying at 188°, whilst the other solidifies at 117·5°, and is practically pure sulphur.

As in the case of the sodium series, this investigation furnished no evidence whatever of the existence of intermediate compounds.

A comparison of the results of this investigation with the work of Biltz and Wilke-Dörfurt (*loc. cit.*) on the polysulphides of rubidium and cæsium is interesting, and brings out more clearly the observation made by the authors in an earlier paper that, whilst the polysulphides of potassium, rubidium, and cæsium resemble one another very closely, the sodium compounds exhibit notable differences. Thus, whilst the three elements first named all form hexasulphides and stable pentasulphides, in the case of sodium no trace of the existence of a hexasulphide could be detected, and the pentasulphide is relatively unstable. On the other hand, sodium tetrasulphide is stable and the trisulphide unstable, this order being reversed for the potassium, rubidium, and cæsium compounds. As regards their appearance, stability, and solidifying points, all the disulphides appear to be similar in character. Towards heat, these compounds show greater stability than any other of the polysulphides of the alkali metals.

For purposes of comparison, the solidifying points of the compounds and eutectic mixtures investigated by the authors, together with the values obtained by Biltz and Wilke-Dörfurt in the rubidium and cæsium series, are given in table III.

TABLE III.

Compound or eutectic.	Sodium.	Potassium.	Rubidium.	Cæsium.
Disulphide	445·0°	471·0°	420·0°	460·0°
Di-tri eutectic	206·0	250·9	200·0	205·5
Trisulphide	223·5	252·0	213·0	217·0
Tri-tetra eutectic	222·6	?(amorphous)	148·5	151·0
Tetrasulphide	275·0	>145·0	>160·0	>160·0
Tetra-penta eutectic	247·6	143·4	159·5	159·5
Pentasulphide	251·8	206·0	231·0	210·0
Penta-hexa eutectic	—	182·9	189·8	178·0
Hexasulphide	—	189·0	201·0	186·0
Saturated solution	249·6	188·1	184·6	172·8

The Molecular Weights of the Polysulphides of Sodium and Potassium in Alcoholic Solution.

The view expressed by Bloxam (*loc. cit.*) that the character of the polysulphides of the alkali metals is better denoted by the general formula R_4S_x than by the usually accepted formula R_2S_x, and that they are to be regarded as derivatives of a compound of the type R_4S_5, has already been referred to. The existence of compounds of the last-mentioned type has not been established by substantial experimental evidence, but the theory was put forward as an attempt to bring the various intermediate compounds which Bloxam claimed to have isolated, of which the so-called enneasulphides are the best examples, into line with those compounds, such as the tetra- and penta-sulphides, the existence of which was generally recognised.

As regards the rubidium and cæsium compounds, Biltz and Wilke-Dörfurt (*loc. cit.*) found no trace of any such intermediate compounds, and the present authors conclude similarly in the cases of the sodium and potassium compounds. Intermediate compounds, if they exist at all, must be of an extremely unstable character.

In order to obtain further evidence as to whether the single or the double formula is to be preferred for these compounds, the molecular weights in alcoholic solution have been determined for such of them as can readily be obtained in the pure state. For this purpose, the ebullioscopic method was employed. Carefully dried alcohol was used, and the polysulphides employed had also remained for several days over phosphoric oxide. In every case their purity was established by analysis.

Several determinations were carried out with each substance, solutions of different concentrations being used. It should be pointed out, however, that owing to the sparing solubilities of sodium sulphide and potassium pentasulphide, it was not possible

in the cases of these substances to vary the concentration of the solutions used to any considerable extent.

The following results were obtained:

Sodium Disulphide.

Number of experiment.	Weight of substance taken. Gram.	Weight of alcohol. Grams.	E.	M.W.	
1	0·2396	32·20	0·098°	70·57	
2	0·3441	31·24	0·173	74·49	Mean = 73·01.
3	0·3684	31·67	0·184	73·97	

Na_4S_4 requires M.W. = 220·28.
Na_2S_2 ,, ,, = 110·14.

Sodium Tetrasulphide.

Number of experiment.	Weight of substance taken. Grams.	Weight of alcohol. Grams.	E.	M.W.	
1	0·2210	31·46	0·071°	115·76	
2	0·4278	30·91	0·152	106·53	Mean excluding
3	0·6194	30·13	0·200	120·26	No. 2 = 119·8.
4	0·8968	30·65	0·290	118·05	
5	1·1836	31·07	0·358	123·07	

Na_4S_8 requires M.W. = 348·56.
Na_2S_4 ,, ,, = 174·28.

Potassium Pentasulphide.

Number of experiment.	Weight of substance taken. Gram.	Weight of alcohol. Grams.	E.	M.W.	
1	0·2761	30·69	0·069°	152·55	
2	0·3478	31·41	0·080	161·94	Mean = 157·25

K_4S_{10} requires M.W. = 467·1.
K_2S_5 ,, ,, = 238·55.

In the case of each polysulphide investigated, the mean observed value for the molecular weight was found to be considerably lower than that required by even the simple formula R_2S_x, and there can therefore be little doubt that under these conditions the double formula is quite out of the question.

The uniformly low results obtained require, however, some further explanation. They may be accounted for in two ways. In the first place, alcoholysis of the solution may occur in accordance with the equation

$$R_2S_x + 2C_2H_5 \cdot OH \rightleftharpoons 2C_2H_5 \cdot OR + H_2S + S_{x-1}.$$
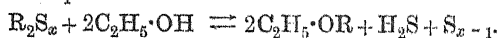
The result of such a reaction would be to reduce the weight of alcohol actually acting as solvent, whilst at the same time the

number of molecules in solution would be increased. Both these results would tend to lower the observed molecular weight.

That alcoholysis does occur to some extent is certain, for in every determination the solution obtained was bright green. This phenomenon has been noted in an earlier paper (T., 1914, **105**, 188), and was there shown to be due to the separation of minute particles of sulphur formed by the decomposition of the polysulphide by alcohol. Since, however, the amounts of hydrogen sulphide given off from such solutions, even during prolonged boiling, were so small as to be practically negligible, the alcoholysis cannot be very considerable.

In the case of sodium tetrasulphide, if one supposes the above equation to represent the reaction and the sulphur produced to be insoluble, the substance would have to be alcoholysed to the extent of more than 45 per cent. in order that the molecular weight might have the observed value. Taking all the known facts concerning the polysulphides of the alkali metals into consideration, this cannot be deemed probable. This opinion is strengthened by the behaviour of sodium tetrasulphide in aqueous solution. One would naturally expect this compound to be decomposed by water to a far greater extent than by alcohol, yet Küster and Heberlein (*loc. cit.*) have shown that in $0.1N$-solution at $25°$ the extent of the hydrolysis is only 11.8 per cent.

On the other hand, the low values obtained by the ebullioscopic method for the molecular weights may be due to the ionisation of the polysulphides in alcoholic solution. Supposing this to be the case, and assuming that the alcoholysis is so slight as to be negligible, in order to account for the difference between the observed and the theoretical values the degree of ionisation must be of the order of 25 per cent.

Turner (*Amer. Chem. J.*, 1908, **40**, 588) has studied the ionisation of alcoholic solutions of various halogen salts of the alkali metals, in particular of potassium iodide. He employed the conductivity method, and the results of his work lead to the conclusion that a $0.1N$-solution of this salt is ionised to the extent of 35 per cent. at its boiling point.

Whilst, therefore, the evidence is insufficient to permit of a definite conclusion being drawn, the authors are of the opinion that, although alcoholysis may in some measure give rise to the observed abnormalities, its effect must be comparatively slight, and the main cause must be looked for in the direction of ionisation of the polysulphide solutions. With the view of gaining further information on this point, the conductivities of alcoholic solutions of the polysulphides will be investigated at a later date.

Summary and Conclusions.

The systems, sodium monosulphide-sulphur and potassium monosulphide–sulphur, have been investigated by a thermo-analytical method, and in each case the existence has been established of a complete series of compounds to which the general formula R_2S_x may be assigned, where x is a whole number having the maximum value 5 in the sodium series and 6 in the case of the potassium series.

No evidence whatever has been obtained of the existence of intermediate compounds, such as the enneasulphide described by Bloxam.

The thermal diagram for the potassium series closely resembles those obtained by Biltz and Wilke-Dörfurt for rubidium and cæsium. In the sodium series, however, the resemblance is much less striking. The sodium compounds differ in appearance and properties, the maximum combining power of the metal is less, and strict parallelism can no longer be observed between this series and the potassium, rubidium, and cæsium series as regards the comparative stabilities of compounds of corresponding compositions. This is in accordance with the behaviour of the alkali metals in their compounds with other elements, notably with iodine.

In connexion with the preparation of the materials necessary for the main research, the rate at which sodium tetrasulphide and potassium pentasulphide lose sulphur when they are heated in a steady stream of hydrogen at regularly increasing temperatures has been investigated. The results obtained lead to the conclusion that the disulphides in each case are extremely stable compounds from which sulphur can only be removed with difficulty.

The bearing of this on the constitution of the polysulphides is of some interest. This question has been discussed by many authors, but the views put forward by Spring and Demarteau (*Bull. Soc. chim.*, 1889, [iii], **1**, 11) and Küster and Heberlein (*Zeitsch. anorg. Chem.*, 1905, **43**, 72) appear to be the most important. The first-mentioned authors point out that whilst towards inorganic substances the polysulphides behave in accordance with the general formula R_2SS_x, their reactions with alkyl haloids are best explained by assuming that they possess the formula $R_2S_2S_x$, in which the first two sulphur atoms in the molecule play quite a different part from the remainder. Spring and Demarteau favour the latter formula, considering the higher polysulphides merely to be solutions of sulphur in the disulphides.

Küster and Heberlein criticise this view on the ground that if it were true, all polysulphides, being essentially salts of hydrogen

disulphide, should be hydrolysed in solution to the same extent, for the hydrolysis could not be influenced by the mere physical solution of sulphur. They consider that the constitutions of the polysulphides and the polyiodides are analogous, and since it is generally recognised that the latter compounds are best represented by the formula RI,I_x, they conclude that the constitution of the polysulphides is best expressed by the formula R_2S,S_x.

With the criticism of Küster and Heberlein the present authors are in agreement. Nevertheless, their results certainly favour the view that in the polysulphide molecule two atoms of sulphur are in a different state of combination from the remainder. They suggest that the disulphides should be regarded as being derived from the form of hydrogen disulphide analogous to the tautomeric form of hydrogen peroxide. They would thus possess the formula $R \cdot S \cdot S \cdot R$. From this substance, the higher polysulphides are obtained, not by solution of sulphur, but by further combination. Thus, the trisulphide would be represented by the formula $\begin{smallmatrix} R \cdot S \vdots S \\ | \\ R \cdot S \end{smallmatrix}$, the tetrasulphide by $\begin{smallmatrix} R \cdot S \vdots S \\ | \\ R \cdot S \vdots S \end{smallmatrix}$, etc.

In this way, the criticism of Küster and Heberlein is obviated, whilst still retaining an explanation of the difference in behaviour of two sulphur atoms in the molecule from that of the remainder.

Taken in conjunction with the work of Biltz and Wilke-Dörfurt, the results of the present investigation establish that the volatilities of the polysulphides of the alkali metals increase with rise in the atomic weight of the metal. This is in agreement with the well-known behaviour of the halogen salts of these metals.

With the object of deciding between the simple formula R_2S_x and the doubled formula R_4S_x, the molecular weights of several polysulphides in alcoholic solution have been determined by the ebullioscopic method. Under these conditions, there can be no doubt that the simpler formula is the correct one. The results obtained were, however, very considerably lower than even the simple formulæ require. The authors attribute this to the ionisation of the solutions, and it is calculated that, assuming alcoholysis to be negligible, such ionisation takes place to the extent of about 25 per cent.

In conclusion, the authors wish to express their thanks to Mr. F. Hughes, who has rendered valuable assistance in the preparation of some of the materials used in the work.

XCV.—*Studies in Catalysis. Part VIII. Thermochemical Data and the Quantum Theory. High Temperature Reactions.*

By WILLIAM CUDMORE McCULLAGH LEWIS.

IT was shown in Part VII. (this vol., p. 457) that, on the basis of the radiation theory, the heat of a reaction is connected with the critical frequencies of the reactants and resultants by the relation :

$$Q = \mathrm{N}h(\Sigma \nu_{\text{resultants}} - \Sigma \nu_{\text{reactants}}),$$

where N is the number of molecules in 1 gram-molecule, h the Planck constant, and ν the critical frequency of any given molecular species taking part in the reaction. It has already been pointed out that this relation was first deduced by Haber (*Ber. Deut. physikal. Ges.*, 1911, **13**, 1117), who also attempted to verify it in three cases, namely, the formation of potassium chloride, potassium iodide, and sodium chloride, from their elements.

In the present paper it is proposed to consider the experimental data available at the present time with the object of obtaining, if possible, a wider experimental basis for the relationship. Incidentally, it is necessary to reconsider Haber's calculations. For our present purpose it is convenient to divide reactions into high temperature reactions and low temperature reactions respectively, indicating by the former that the chemical changes require quanta of great size, corresponding with the visible and ultra-violet regions of the spectrum, indicating by the latter that the reactions are such that quanta belonging to the short infra-red region are sufficient to account for the critical increments involved.

High Temperature Reactions.

As examples of this class we are concerned mainly with the heats of formation of inorganic salts. To test the relation already given, it is necessary to know the critical frequency of each of the substances participating in the reaction. In a large number of cases these frequencies have not yet been directly observed. Haber (*loc. cit.*) has suggested, however, a very simple relation, which, although semi-empirical, may be employed in this connexion. This relation, which will be referred to as the square-root rule, states that the characteristic infra-red frequency, ν_r, of a substance, that is, the frequency of the residual ray which is capable of accounting approximately for the specific heat of the substance, is connected

with the characteristic frequency, ν_v, in the ultra-violet region in the following way:

$$\frac{\nu_v}{\nu_r} = \sqrt{\frac{M}{m}},$$

where m is the mass of an electron and M is the molecular weight of the substance. The ultra-violet frequency, ν_v, referred to is that which corresponds with the maximum of the selective photo-electric effect. Employing the atomic weight for M in the case of a number of elements, the alkali metals, Haber has shown that the calculated and observed frequencies agree satisfactorily.

Haber has extended the application of the square-root rule to the calculation of the characteristic ultra-violet frequency of solid compounds (salts). Thus, in the case of rock salt, Rubens and Aschkinass have observed the characteristic infra-red band at $51\cdot2\,\mu$. Taking M as $58\cdot46$, the normal molecular weight of sodium chloride, the ultra-violet wave-length thus calculated is $156\cdot4\,\mu\mu$, which agrees extremely well with the value, $156\cdot3\,\mu$, obtained by Martens from dispersion measurements. In the case of potassium chloride, the infra-red band occurs at $61\cdot1\,\mu$, whence, employing the normal molecular weight of the salt in the square-root rule, Haber finds that the ultra-violet wave-length is $165\cdot3\,\mu\mu$, whilst Martens obtained $160\cdot7\,\mu\mu$ from the dispersion. The values quoted are those given by Haber. So far as these data go, they indicate the general applicability of the rule. Haber further points out that, in addition to the characteristic ultra-violet frequencies referred to in the above cases, the dispersion measurements indicate the existence of a still shorter wave-length. It is an interesting fact, although not bearing directly on the present problem, that these shorter wave-lengths may also be calculated with considerable accuracy by means of the square-root rule, provided we employ twice the molecular weight of the salt, for the quantity M. Thus, in the case of rock salt, the second ultra-violet absorption band is calculated to be $110\cdot6\,\mu\mu$, whilst Martens's value, obtained from dispersion data, is $110\cdot7\,\mu\mu$. In the case of sylvine, Haber calculates, in a similar manner, that the shorter ultra-violet dispersional band should occur at $116\cdot7\,\mu\mu$, whilst Martens has calculated the value $115\cdot3\,\mu\mu$.

As already mentioned, Haber has applied the square-root relation to elements such as the alkali metals and to iodine, in which M is taken to represent the *atomic* weight, with satisfactory results. In the case of iodine, M obviously represents one-half of the molecular weight of the substance in the dissolved or gaseous state. In general, therefore, the term M may refer to the normal molecular weight, or to one-half this quantity. That the relation is largely empirical is evidenced by this lack of precision as to the significance of M,

especially when we consider that the investigation of the solid state by means of the X-ray spectrometer has led to a quite new conception of the molecular weights of solids.

It would appear that in the large majority of salts the term M denotes the usually accepted value for the molecular weight. It will be shown later, however, that one-half of the molecular weight appears to be the correct quantity to employ in the case of the thallium haloids .

The significance to be attached to M is not entirely arbitrary. The following considerations serve as a guide. If we restrict ourselves to the chlorides, bromides, and iodides of a given metal, we would expect on general grounds to find a certain sequence in the ultra-violet frequencies, such as is found in the far infra-red region (compare Rubens and von Wartenberg, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 169). That is, we would expect the bromide to occupy an intermediate position between the chloride and iodide. In the case of the thallium haloids, using the normal molecular weights, we obtain for the ultra-violet frequencies, $15 \cdot 52 \times 10^{14}$ for the chloride, $18 \cdot 3 \times 10^{14}$ for the bromide, and $15 \cdot 21 \times 10^{14}$ for the iodide. Using the half-molecular weights, the corresponding values are: $15 \cdot 21 \times 10^{14}$, $12 \cdot 93 \times 10^{14}$, and $10 \cdot 76 \times 10^{14}$. In the first case the sequence is broken, in the latter it remains. We conclude, therefore, that the latter values are more nearly correct. It will be shown later that the conclusions, here tentatively drawn, are borne out from the point of view of the heat determinations.

In Haber's consideration of the heats of formation of salts the process is regarded as involving the removal of electrons from certain atoms and their addition to others. Haber visualises the process in the following way for the union of a halogen with an alkali metal.

Let us imagine an electric space lattice containing halogen atoms and atoms of the metal which have not yet reacted with one another to give the solid salt. The electric space lattice is supposed to possess properties which may be regarded as the mean of those exhibited by solid halogen and solid metal separately. This mean or average state is then characterised by the single ultra-violet frequency, $(v_1 + v_2)/2$, where v_1 is the frequency of the alkali metal by itself and v_2 is that of the solid halogen. When transfer of the electron has taken place, the nature of the space lattice is altered, the frequency being now that of the alkali salt. Haber then proceeds to determine whether the work * term, hv, involved in the removal of

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* Haber regards the quantum as measuring the work of removing an electron. It would appear more justifiable to identify the quantum with the total energy change involved in the transfer of the electron.

an electron from the alkali haloid salt space lattice, is equal to the heat of formation reckoned per gram-molecule, together with the work term $h(0.5\nu_1 + 0.5\nu_2)$.

The first case considered by Haber is that of potassium iodide. The heat evolved by the union of the solid elements to produce the solid salt is 80,100 cals. per gram-molecule of the salt. Pohl and Pringsheim have observed the selective photo-electric effect of potassium, the frequency being $\nu_K = 0.685 \times 10^{15}$. From measurements of the atomic heat of iodine, it follows that the characteristic iodine frequency in the infra-red is 2.0×10^{12}. Employing the square-root rule, with $M = 127$, Haber calculates the ultra-violet frequency of solid iodine to be $\nu_1 = 0.9646 \times 10^{15}$. Hence,

$$Nh(0.5\nu_1 + 0.5\nu_K) = 79,630 \text{ cals.}$$

The heat of union of K and $I = 80,100$,,

Hence, for the salt, $Nh\nu_{KI} = 159,730$,,

From this result Haber calculates the ultra-violet frequency of the salt to be 1.654×10^{15}. Applying the square-root rule, in the inverse manner, Haber calculates from this value the characteristic frequency of the salt in the far infra-red region. The result, expressed in wave-length, is 100 μ. The value observed by Rubens (*loc. cit.*, 1914) is 94·1 μ. The agreement is fairly good.

Haber next considers the formation of sodium chloride. The heat of reaction between solid chloride and sodium is taken to be 94,600 cals. The ultra-violet frequency of rock salt, obtained from dispersion measurements, is 1.918×10^{15} or $\lambda_\nu = 156.4 \mu\mu$. This corresponds with the value 185,200 cals. for $Nh\nu_{NaCl}$, the radiant energy required to activate one gram-molecule of the salt. Subtracting the heat of formation from this quantity, we find the value of $(0.5\nu_{Cl} + 0.5\nu_{Na})$, namely, 0.9382×10^{15}, for half the sum of the frequencies of sodium and chlorine. On doubling this value and subtracting from it the ultra-violet frequency of sodium, which Pohl and Pringsheim have found by experiment to be $\nu_{Na} = 0.947 \times 10^{15}$,[*] we obtain the value $\nu_{Cl} = 0.9294 \times 10^{15}$ for the ultra-violet frequency of solid chlorine. Haber uses this to calculate the density of solid chlorine, employing a relation of Lindemann, and finds a number of the order which would be anticipated. This, however, is not a rigid test. Haber, therefore, considers the two following reactions simultaneously: $K + Cl = KCl$ and $Na + Cl = NaCl$. On subtracting the second equation from the first, we obtain:

$$K + NaCl = KCl + Na.$$
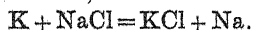
[*] The above value is that quoted by Haber. The corresponding wave-length is 317 $\mu\mu$. Recent measurements by Pohl and Pringsheim, however, give the value 340 $\mu\mu$ for the maximum of the selective photo-electric effect of sodium (compare Hughes, "Photo-electricity," p. 84).

The corresponding energy expressions are:

$$Nh[\nu_{KCl} - 0\cdot5(\nu_K + \nu_{Cl})] = Q_{KCl}.$$
$$Nh[\nu_{NaCl} - 0\cdot5(\nu_{Na} + \nu_{Cl})] = Q_{NaCl}.$$

which give on subtraction

$$Nh(\nu_{KCl} - \nu_{NaCl} - 0\cdot5\nu_K + 0\cdot5\nu_{Na}) = Q_{KCl} - Q_{NaCl}.$$

If we now write $\nu_K = 0\cdot685 \times 10^{15}$, $\nu_{NaCl} = 1\cdot918 \times 10^{15}$, $\nu_{Na} = 0\cdot947 \cdot 10^{15}$, we can calculate the ultra-violet frequency of sylvine. The value thus obtained is $1\cdot8683 \times 10^{15}$ or $\lambda_c = 160\cdot5 \mu\mu$, which is in excellent agreement with the value calculated by Martens from dispersion measurements, namely, $160\cdot7 \mu\mu$.

Reviewing Haber's treatment of the problem, it is evident that considerable doubt exists as regards the mechanism whereby he the sum of the frequencies of the halogen and metal is introduced, although it is evident that the results obtained by this means are in good agreement with the observed values. On the basis of the expression for the heat of a reaction, quoted at the beginning of this paper, we should have expected the sum of these two quantities, not half the sum. Haber's concept of the mechanism of union of the halogen atom with the atom of the alkali metal seems to involve a rather artificial mean stage, which is itself regarded as the starting point of the process.

An alternative view might be taken of the mechanism, and this view has the advantage that it does not restrict us to the solid state only. If we suppose that the ultra-violet quantum, corresponding with the selective photo-electric effect, breaks the bond between two adjacent atoms, that is, activates two atoms in a chemical sense, then one quantum characteristic of sodium plus one quantum characteristic of chlorine serves to bring about the following reaction: $2Na + 2Cl = 2NaCl$. Hence the heat of formation, $2Q$, reckoned for two gram-molecules of the salt, would be given by

$$[2Nh\nu_{NaCl} - (Nh\nu_{Na} + \nu_{Cl})],$$

or the heat of formation of one gram-molecule is given by

$$[Nh\nu_{NaC} - 0\cdot5Nh(\nu_{Na} + \nu_C)],$$

which is simply Haber's expression, without any assumption being made as to a mean stage.

Dissociation of the Halogens.

The dissociation of chlorine, bromine, and iodine may be considered before the question of the formation of salts, as the data are required for later calculations.

It will be observed that the relation

$$Q = Nh(\Sigma\nu_{\text{resultants}} - \Sigma\nu_{\text{reactants}})$$

is identical with $Q = (E_{\text{resultants}} - E_{\text{reactants}})$.

where E stands for the critical increment as defined in previous papers.

In the case of gaseous iodine and bromine, Evans (*Astrophys. J.*, 1910, **32**, I, 291) has found that, on raising the temperature, the bands in the visible region finally disappear, the lowest observed temperature of disappearance being 950°. The temperature of disappearance of colour is a function of the pressure of the gas, the greater the pressure the higher being the temperature of disappearance. In view of this behaviour, Evans has concluded that the disappearance of colour is due to dissociation into atoms, which evidently do not absorb in the visible region. The atoms must absorb either in the ultra-violet or the infra-red region.

The heat of dissociation of the halogens is negative, heat being absorbed in the process. In order that Q may be negative, the critical increment of the reactant (molecular form) must be greater than the increment of the resultant (atomic form). Hence, on taking Evans's results into account, and applying the radiation expression, we conclude that the critical increments of the atoms correspond with quanta in the infra-red region. Further, the heats of dissociation represent quantities of energy considerably greater than those obtainable from the infra-red region. It is obvious that, in the case of gaseous dissociation, the critical increment of the reactant must exceed the observed heat of dissociation. If, however, the critical increments of the resultants are small, as in the present case, the heat of dissociation cannot be very different from the critical increments of the corresponding undissociated molecules.

The observed heats of dissociation per gram-molecule at a fairly high temperature, that is, at a temperature at which the dissociation becomes measurable, are in round numbers as follow: chlorine, $-113,000$ cals. (compare Pollitzer, Ahrens "Sammlung," 1912, **17**, 434); bromine, $-50,000$ cals. (Bodenstein and Cramer, *Zeitsch. Elektrochem.*, 1916, **22**, 327); iodine, $-36,860$ cals. (Bodenstein and Starck, *ibid.*, 1910, **16**, 961).

The values in the case of bromine and iodine are known with considerable exactness; that for chlorine is a rough approximation only. From a consideration of the temperature range at which these gases dissociate sensibly, it is evident that we are dealing with high temperature reactions, that is, reactions which require larger quanta than those which correspond with the short infra-

red region.   Further, iodine dissociates more easily than bromine
and bromine more easily than chlorine.   We would expect, there
fore, that the critical energy, and hence the size of the correspond
ing quantum, would increase in the order: iodine, bromine,
chlorine.   This sequence is also exhibited by the values of the
respective heats of dissociation.

To show that radiation in the visible region is capable of sup-
plying quanta of the necessary size, we may proceed in the follow-
ing approximate manner.   As indicated by its violet colour, iodine
absorbs largely in the red end of the visible spectrum.   Assuming
that the characteristic wave-length is of the order $700 \mu\mu$, it follows
that the critical increment per gram-molecule is 41,000 cals. in
round numbers.   This is slightly greater than the observed heat
of dissociation.   It is therefore a possible value.   Similarly, if we
take the wave-length $500 \mu\mu$ to be characteristic of bromine, this
wave-length corresponding with absorption in the green region, we
find the critical increment per gram-molecule to be 57,000 cals.
This quantity is somewhat greater than the observed heat of dis-
sociation of bromine.   Owing to the very extensive absorption of
both iodine and bromine throughout the visible region, it is
impossible at the present time to ascribe the critical increment to
any particular band.   The investigations of Hasselberg and of
Konen (compare Konen, *Ann. Phys. Chem.*, 1898, [iii], **65**, 257)
show that iodine possesses numerous bands in the visible region.
The same is probably true of bromine, although a recent investiga-
tion by Peskov (*J. Physical Chem.*, 1917, **21**, 382) indicates a
broad maximum at $436 \mu\mu$, with considerable absorption down to
$600 \mu\mu$.   In the case of chlorine, a well-defined band has been
measured by Brannigan and Macbeth (T., 1916, **109**, 1277) in the
near ultra-violet occurring at λ $327 \mu\mu$.   Peskov (*loc. cit.*) places
the maximum at $334 \mu\mu$.   Taking Brannigan and Macbeth's value,
it is found that the critical increment of chlorine is 86,750 cals.
per gram-molecule.   This is considerably less than the value quoted
for the heat of dissociation, but it is to be remembered that the
latter is a rough approximation, and the quantity 86,750 is
theoretically an upper limit for the heat effect.   We require the
critical increments of the halogens in the gaseous state in dealing
subsequently with the formation of salts.   For this purpose, we
shall employ the following average values: chlorine, 86,750 cals.
per gram-molecule; bromine, 57,000 cals.; and iodine, 41,000 cals.

It may be mentioned that the process of dissociation of chlorine,
bromine, and iodine is one which requires larger quanta than are
required for the decomposition of the corresponding halogen hydr-
acids.   The only exact measurements available in this connexion

refer to hydrogen iodide, for which the critical increment per gram-molecule is 20,000 cals., a quantity which corresponds with the short infra-red region.

Heat of Formation of Salts

Potassium Chloride.

The characteristic ultra-violet frequency of this salt, as obtained from dispersion measurements, is $18 \cdot 6 \times 10^{14}$, or $\lambda_v = 160 \cdot 3\,\mu\mu$. The value of the critical increment $Nh\nu_{KC}$ is therefore 175,960 cals. per gram-molecule. As regards the critical increment of potassium, the maximum of the selective photo-electric effect occurs at $\lambda = 440\,\mu\mu$, whence the increment is 64,517 cals. This amount of energy, on the view already suggested, represents the amount required to activate two adjacent atoms of potassium. The stoicheiometric equation requires one-half of this quantity. Similarly, the critical increment of one gram-molecule of chlorine or two gram-atoms of chlorine is 86,750 cals. The total critical increment of one gram-atom of each reactant is $(64,517 + 86,750)/2$, or 75,634 cals. Applying the equation

$$Q = Nh\nu_{\text{resultant}} - Nh\nu_{\text{reactant}}.$$

it follows that $Q = 175,960 - 75,634 = +100,330$ cals. in round numbers, whilst Q, observed (Thomsen) $= +105,600$ cals. Hackspill ("Tables Annuelles," **3**, p. 588) gives the value 99,650 cals. for the heat of formation. The agreement between observed and calculated values is moderately good. It may be mentioned that if the square-root rule had been employed, with $M = 74 \cdot 5$, in the case of the salt and the infra-red frequency as determined by Rubens, the critical increment per gram-molecule would have been 164,000 cals., which is somewhat lower than that obtained from dispersion measurements. As regards the observed heats of formation of salts, it may be pointed out that the values given are in general obtained indirectly, so that the result is liable to a certain amount of error.

Potassium Bromide.

The characteristic infra-red band, as observed by Rubens (compare Rubens and von Wartenberg, Sitzungsber. K. Akad. Wiss., Berlin, 1914, 169), occurs at $\lambda = 82 \cdot 6\,\mu$. Measurements of the molecular heat of the salt require the wave-length $82 \cdot 4\,\mu$ (Nernst, Ann. Physik, 1911, [iv], **36**, 395) in the Nernst-Lindemann formula, that is, $\nu_r = 0 \cdot 036 \times 10^{14}$. Using the square-root rule and

the normal molecular weight of the salt, the ultra-violet frequency $\nu_v = 16 \cdot 67 \times 10^{14}$, or $\lambda_r = 180 \, \mu\mu$. Hence the critical increment, $Nh\nu_{KBr}$, per gram-molecule is 157,700 cals. As before, the energy required for two gram-atoms of potassium is 64,517 cals. For bromine, the critical increment for two gram-atoms is 57,000 cals. Hence for the formation of one gram-molecule of the salt, the total critical increment of the reactants is $(64{,}517 + 57{,}000)/2 = 60{,}758$ cals. Hence

$$Q = 157{,}700 - 60{,}758 = +96{,}940 \ \text{cals.}$$

The observed heat of reaction between liquid bromine and solid potassium is $+95{,}310$ cals. The calculated value refers to gaseous bromine, so that it is necessary to add the heat of vaporisation of bromine, namely, 3500 cals., to the observed value, thereby obtaining the quantity 98,810 cals. The agreement between calculated and observed values is moderately good.

Sodium Chloride.

The observed infra-red band of the salt occurs at $52 \, \mu$. The value $51 \, \mu$ is required to account for the molecular heat (compare Nernst, *loc. cit.*). The infra-red frequency is therefore $0 \cdot 0577 \times 10^{14}$. Using the square-root rule and the normal molecular weight of the salt, the ultra-violet frequency $\nu_v = 19 \cdot 27 \times 10^{14}$, or $\lambda_r = 155 \, \mu\mu$, which agrees excellently with the value calculated from dispersion measurements. It follows that the critical increment, $Nh\nu_{NaCl}$, per gram-molecule of the salt is 182,290 cals. The critical increment of two atoms of sodium is obtained from the position of the selective photo-electric effect which occurs at $\lambda = 340 \, \mu\mu$, or $\nu_{Na} = 8 \cdot 8 \times 10^{14}$, the value of the increment being 83,250 cals. Hence the total critical increment of one gram-atom of sodium and one gram-atom of chlorine is $(83{,}250 + 86{,}750)/2$, or 85,000 cals. Hence,

$$Q = 182{,}290 - 85{,}000 = 97{,}290 \ \text{cals.}$$
$$Q \ \text{(observed)} \qquad = 97{,}800 \quad \text{,,}$$

The agreement is good.

Potassium Iodide.

It has already been pointed out that Haber demonstrated the validity of the heat expression in connexion with this substance. Haber considers the reaction as taking place between the elements in the solid state. For iodine, he makes use, therefore, of the square-root rule to calculate the characteristic ultra-violet fre-

quency. On the other hand, considering the reaction between gaseous iodine and solid potassium, and employing therefore the value 41,000 cals. for the critical increment of two gram-atoms of iodine vapour, the agreement between the observed and the calculated heat effect is far from satisfactory. We are dependent, of course, upon the correctness of the infra-red characteristic frequency of the salt, which has been observed to occur at $\nu_r = 0\cdot0319 \times 10^{14}$. Using the square-root rule and the normal molecular weight of the salt, we obtain for the ultra-violet frequency the value $17\cdot45 \times 10^{14}$, or $\lambda_v = 172\,\mu\mu$, whence $Nh\nu_{KI} = 165,077$ cals. Employing the values already given for the critical increments of solid potassium and iodine vapour, the calculated heat effect is 112,320 cals., whilst the observed is 83,100 cals. The discrepancy is very great. If we employ one-half of the normal molecular weight of the salt in the square-root rule, we obtain, finally, the value 63,680 cals. for the calculated heat of the reaction. This is, now, considerably less than the observed value. There does not appear to be any justification, however, for this mode of calculation in view of the results obtained in the case of the other alkali haloids, in which the normal molecular weight of the salt is employed. The agreement obtained by Haber rests on the fact that in the case of iodine he applied the square-root rule to the infra-red frequency given by Lindemann's melting-point formula. The resulting value for the critical increment for solid iodine is 91,300 cals. The value which we have taken for gaseous iodine is widely different, namely, 41,000 cals.

It may be pointed out, however, that the value $\lambda_v = 172\,\mu\mu$ for the ultra-violet wave-length of the salt—a quantity which is employed by Haber and by the author—is almost certainly incorrect, as it involves a breaking down in the expected sequence of the chloride, bromide, and iodide. Thus, since $\lambda_{KCl} = 160\cdot7\,\mu\mu$ and $\lambda_{KBr} = 180\,\mu\mu$, we should expect λ_{KI} to lie somewhere in the region of $200\,\mu\mu$. If we take the observed value for the heat of formation, together with the critical increments of solid potassium and gaseous iodine already employed, we can calculate the critical increment of the salt. The value thus obtained is 135,860 cals. per gram-molecule. It follows from this that the ultra-violet frequency of the salt is $14\cdot4 \times 10^{14}$, or $\lambda_{KI} = 208\,\mu\mu$. This value occupies, roughly, the expected position with respect to potassium chloride and potassium bromide, but at the present time there is no means of further testing its accuracy. Taking this value to be correct, and applying the square-root rule in the inverse sense, we find that the characteristic infra-red wave-length is $115\,\mu$.

Silver Chloride.

The observed infra-red band of the salt occurs at $\lambda = 81\cdot5\,\mu$. Hence $\nu_r = 0\cdot0368 \times 10^{14}$. Using the square-root rule and the normal molecular weight of the salt, we obtain for the ultra-violet frequency $\nu_v = 18\cdot66 \times 10^{14}$, or $\lambda_v = 160\,\mu\mu$. That is, $Nh\nu_{AgCl} = 166{,}520$ cals. For silver, the infra-red frequency given by Biltz (*Zeitsch. Elektrochem.*, 1911, **17**, 676), on the basis of the Lindemann melting-point formula, is $\nu_r = 0\cdot0436 \times 10^{14}$ (compare also Lindemann, *Ber. Deut. physikal. Ges.*, 1911, **13**, 1114). Using the square-root rule with $M = 108$, we obtain for the ultra-violet frequency $\nu_v = 19\cdot23 \times 10^{14}$, or $\lambda_v = 156\,\mu\mu$. The corresponding value of $Nh\nu_{Ag}$ is $182{,}016$ cals. for the activation of two gram-atoms. Hence the total critical increment of one gram-atom of each of the reactants is $(182{,}016 + 86{,}750)/2$, or $134{,}383$ cals. Hence $Q = 166{,}520 - 134{,}383 = 32{,}140$ cals., whilst Q, observed (Fischer, *Zeitsch. Elektrochem.*, 1912, **18**, 283) $= 29{,}940$ cals. The agreement is moderate.

Silver Bromide.

The observed infra-red band of the salt occurs at $127\,\mu$, or $\nu_r = 0\cdot0266 \times 10^{14}$. Proceeding as in the previous case, the ultra-violet frequency is $15\cdot48 \times 10^{14}$, or $\lambda_v = 194\,\mu\mu$. Hence $Nh\nu_{AgBr} = 146{,}440$ cals. From the data already given, it follows that the critical increment of the reactants per gram-atom of each is $(182{,}016 + 57{,}000)/2 = 119{,}508$ cals. Hence the heat of formation $Q = 146{,}440 - 119{,}508 = 26{,}930$ cals. in round numbers. The observed heat of formation for liquid bromine and solid silver is $22{,}700$ cals. Hence for the reaction involving gaseous bromine the observed heat is $26{,}200$ cals., which is in good agreement with the calculated value. In all cases, the calculated heat effect is a relatively small difference between two large quantities. It is not to be expected, in general, that the result can be an accurate one.

Silver Iodide.

The characteristic infra-red band of this salt has not yet been measured. It is possible, however, to obtain a moderately exact value by comparing the observed values of the three thallium haloids with the two silver haloids, all of which have been measured by Rubens. These are as follows: TlCl, $91\cdot6\,\mu$; TlBr, $117\cdot0\,\mu$; TlI, $151\cdot8\,\mu$. For the silver haloids: AgCl, $81\cdot5\,\mu$; AgBr, $112\cdot7\,\mu$. On plotting these figures, the lines run approxim-

ately parallel, and an extrapolation indicates $\lambda = 145\,\mu$ for silver iodide. This value is probably correct to ±5 per cent. The infra-red frequency is therefore $0\cdot0207 \times 10^{14}$. Using the square-root rule and the normal molecular weight of the salt, the ultra-violet frequency is $13\cdot46 \times 10^{14}$, or $\lambda_v = 223\,\mu\mu$. Hence $Nh\nu_{AgI} = 127{,}332$ cals. Employing the values already obtained for silver and gaseous iodine, the total critical increment of the reactants per gram-atom is $(182{,}016 + 41{,}000)/2 = 111{,}508$ cals. Hence the heat formation $Q = 127{,}332 - 111{,}508 = +15{,}820$ cals. in round numbers. The heat of formation of the salt from the elements in the solid state has been accurately measured by Fischer (*loc. cit.*), the value being $+15{,}100$ cals. Taking the heat of sublimation of iodine to be 3000 cals. per gram-atom, the observed heat of the reaction involving gaseous iodine is 18,100 cals., which agrees approximately with that calculated on the radiation theory.

It will be observed that in the above calculation we have made use of the value 41,000 cals. for the gram-molecular increment of gaseous iodine. Had we employed the value 91,300 cals. obtained from the infra-red band by means of the square-root rule (which Haber has employed in the case of potassium iodide), the heat of the reaction between the *solid* elements calculated on this basis would have been a negative quantity, namely, -9300 cals., in place of the observed positive quantity, $+15{,}100$ cals. This further emphasises the difficulty met with in the formation of potassium iodide. The result serves to throw still further doubt on the value $172\,\mu\mu$ as being the ultra-violet wave-length of potassium iodide.

Thallium Haloids.

Thallium Chloride.—Direct measurement of the infra-red band of the salt gives the value $\lambda = 91\cdot6\,\mu$, or $\nu_r = 0\cdot0327 \times 10^{14}$. Using the square-root rule and the normal molecular weight, the value obtained for the ultra-violet frequency is $15\cdot52 \times 10^{14}$, or $\lambda_v = 193\,\mu\mu$. Hence $Nh\nu_{TlCl} = 146{,}820$ cals. For thallium metal, Biltz (*loc. cit.*), gives the value $\nu_r = 0\cdot0184 \times 10^{14}$. Using the square-root rule, the ultra-violet frequency $\nu_v = 11\cdot15 \times 10^{14}$, or $\lambda_v = 269\,\mu\mu$. The value of $Nh\nu_{Tl}$ for two gram-atoms of the metal is therefore 105,480 cals. Hence the critical increment of the reactants, per gram-atom, is $(105{,}480 + 86{,}750)/2 = 96{,}115$ cals., and the heat of formation $Q = 146{,}820 - 96{,}115 = 50{,}700$ cals. in round numbers. The observed heat of formation is 48,600 cals. The agreement is satisfactory.

Thallium Bromide.—The infra-red band occurs at $\lambda = 117\,\mu$, or $\nu_r = 0\cdot0256 \times 10^{14}$. Using the square-root rule and the normal

X X*

molecular weight, we obtain for ν_v the value $18\cdot3 \times 10^{14}$, or $\lambda_v = 164\,\mu\mu$. Hence $Nh\nu_{Br} = 173,120$ cals. The critical increment of thallium and of bromine have already been given. The total critical increment of the reactants is $(105,480 + 57,000)/2$, or $82,240$ cals. Hence $Q = 173,120 - 82,240 = 90,880$ cals. The observed heat effect for the reaction involving liquid bromine is 41,300 cals., and therefore for gaseous bromine 44,800 cals. The discrepancy is very great.

Thallium Iodide.—The infra-red band occurs at $151\cdot8\,\mu$, or $\nu_r = 0\cdot0197 \times 10^{14}$. Using the square-root rule and the normal molecular weight of the salt, we obtain $\nu_v = 15\cdot21 \times 10^{14}$, or $\lambda_v = 197\,\mu\mu$. Hence $Nh\nu_{TlI} = 143,890$ cals. The critical increment of the reactants is $(105,480 + 41,000)/2 = 73,240$ cals. Hence $Q = 143,890 - 73,240 = 70,650$ cals., whilst Q, observed, is 30,200 cals. As this refers to solid iodine, the observed value for the reaction involving gaseous iodine is 33,200 cals. The discrepancy is even greater than in the case of the bromide.

It has already been pointed out, however, that the values obtained for the ultra-violet frequencies of the thallium haloids suggests that the square-root rule should be employed in conjunction with *half* the molecular weight of the salt, in order to give the correct sequence in the ultra-violet frequencies of the three salts. Carrying out the calculation, we obtain the following results:

Thallium Chloride.—$\nu_{TlCl} = 15\cdot21 \times 10^{14}$, or $\lambda_v = 197\,\mu\mu$. Hence $Nh\nu$ for the salt is 143,890 cals., and therefore $Q = 47,780$ cals., whilst the observed value is 48,600 cals.

Thallium Bromide.—$\nu_{TlBr} = 12\cdot93 \times 10^{14}$, or $\lambda_r = 232\,\mu\mu$. Hence $Nh\nu$ for the salt is 122,320 cals., and therefore $Q = 40,080$ cals., whilst Q, observed, is 44,800 cals.

Thallium Iodide.—$\nu_{TlI} = 10\cdot76 \times 10^{14}$, or $\lambda_r = 278\,\mu\mu$. Hence $Nh\nu = 101,790$ cals., and therefore $Q = 28,550$ cals. The observed value is 33,200 cals. All three thallium haloids exhibit satisfactory agreement between the observed and calculated heats of formation, on the assumption that one-half of the molecular weight should be employed in conjunction with the square-root rule. This is scarcely likely to be accidental, although no reason for the choice can as yet be given.

Lead Chloride.

The characteristic infra-red band of lead chloride has been observed by Rubens at $\lambda_r = 91\cdot0\,\mu$, that is, $\nu_r = 0\cdot033 \times 10^{14}$. Using the normal molecular weight, we obtain for the ultra-violet frequency $\nu_v = 23\cdot33 \times 10^{14}$, whence the critical increment per gram-

molecule is 220,700 cals. The infra-red frequency for metallic lead is $0·0195 \times 10^{14}$ (Nernst, *loc. cit.*), whence the ultra-violet frequency is $11·9 \times 10^{14}$, or $\lambda_v = 252 \,\mu\mu$; whence the critical increment of two gram-atoms is 112,574 cals. and the increment per gram-atom is 56,290 cals. The critical increment per gram-molecule (Cl_2) is 86,750 cals. Hence the heat of formation of one gram-molecule of lead chloride is $220,700 - (56,290 + 86,750) = 77,660$ cals. The observed heat of formation (involving gaseous chlorine) is $+ 85,570$ cals. according to Braune and Koref (*Zeitsch. Elektrochem.*, 1912, **18**, 818), and 85,380 cals. according to Günther (*ibid.*, 1917, **23**, 197). The agreement is only approximate, the discrepancy being due probably to error in the value taken for the critical increment of the salt. Assuming the observed value of Braune and Koref, we can calculate a 'corrected' value for the critical increment of the salt, namely, 228,610 cals. By applying the square-root rule, we find the infra-red frequency to be $0·034 \times 10^{14}$, or $\lambda_r = 89·2 \,\mu$, which is not greatly different from that observed by Rubens ($91·0 \,\mu$). This illustrates how sensitive the final value for the heat effect is to error in the infra-red frequency.

Mercuric Chloride.

The infra-red band of the salt occurs at $95 \,\mu$. Employing the normal molecular weight, the ultra-violet frequency is found to be $22·06 \times 10^{14}$, or $\lambda_v = 136 \,\mu\mu$. The critical increment is therefore 208,690 cals. per gram-molecule. The corresponding quantity for one gram-molecule of chlorine is 86,750 cals. Lindemann (*loc. cit.*) finds the infra-red frequency of mercury to be $0·022 \times 10^{14}$, whence the ultra-violet frequency is $13·2 \times 10^{14}$, or $\lambda_v = 227 \,\mu\mu$. Hence the critical increment of mercury is 124,872 cals. for two gram-atoms, or 62,436 cals. per gram-atom. The heat of formation per gram-molecule of mercuric chloride is therefore

$$208,690 - (86,750 + 62,436) = 59,504 \text{ cals.}$$

The observed heat of the reaction between liquid mercury and gaseous chlorine is 53,300 cals. Lindemann's value for the infra-red frequency refers to solid mercury. On correcting for the latent heat of fusion, the calculated heat of the reaction is 59,000 cals.

Mercurous Chloride.

Let us assume, in the first place, that the molecule of the salt is represented by HgCl. The observed infra-red band is $98·8 \,\mu$, or $\nu_{,v} = 0·0304 \times 10^{14}$. Using the normal molecular weight, we find $\nu_v = 19·76 \times 10^{14}$, or $\lambda_v = 152 \,\mu\mu$, whence the increment is 186,930

cals. per gram-molecule. The critical increment per gram-atom of mercury we have already taken to be 62,436 cals., the corresponding quantity per gram-*atom* of chlorine being 43,375 cals. Hence the heat of formation of the salt is $186,930 - (43,375 + 62,436) =$ 81,120 cals. The observed heat of formation (Nernst, *Zeitsch. physikal. Chem.*, 1888, **2**, 23) is 31,300 cals. The discrepancy is very great.

Let us now assume that the salt is represented by the formula Hg_2Cl_2. Using the square-root rule with this molecular weight, we find $\nu_v = 27 \cdot 97 \times 10^{14}$, or $\lambda_v = 107 \mu\mu$. Hence the increment is 264,600 cals. The reaction is now represented by $2Hg + Cl_2 = Hg_2Cl_2$, hence the critical increment of the reactants is double the value given above. The heat of formation is thus calculated to be $264,600 - 211,620 = 53,000$ cals. in round numbers. As the observed heat of reaction refers to one-half the quantities here considered, it is necessary to calculate the heat effect per gram-atom of mercury, namely, 26,500 cals. This is in much better agreement with the observed value than the result obtained by the previous method. It appears, therefore, that the correct formula is Hg_2Cl_2, and not $HgCl$, a conclusion which is borne out by measurements on the salt in the dissolved state. Employing the observed value for the heat effect, we can calculate a 'corrected' value for the increment of the salt, namely, 274,000 cals. in round numbers. Thence, calculating backwards, we obtain the value $\nu_r = 0 \cdot 0302 \times 10^{14}$, or $\lambda_r = 101 \mu$, for the salt, which is not very different from the observed value ($98 \cdot 8 \mu$).

The Reaction: $Pb + 2AgCl = PbCl_2 + 2Ag$.

The heat of this reaction per gram-atom of lead is, according to Magnus (*Zeitsch. Elektrochem.*, 1910, **16**, 273), 24,590 cals. As we have already obtained the critical increments for the substances participating in this reaction, it should be possible to calculate the heat effect. Thus:

Increment for two gram-molecules of AgCl ...	$=$	$2 \times 166,520$ cals.
„ „ one gram-atom of lead	$=$	56,290
Hence, total critical increment of reactants	$=$	389,330 cals.
Increment for one gram-molecule of $PbCl_2$ ...	$=$	228,610
„ „ two gram-atoms of silver	$=$	182,016
Hence, total critical increment of resultants	$=$	410,626 cals.

Hence $Q = 410,626 - 389,330 = +21,300$ cals. in round numbers. This is of the correct order of magnitude, and the result is satisfac-

tory in view of the fact that we are dealing with a small difference between two very large quantities.

The Reaction: $Pb + Hg_2Cl_2 = PbCl_2 + 2Hg$.
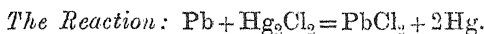
Proceeding as in the previous case, we obtain:

Increment for one gram-atom of lead	$= 56,290$
,, ,, gram-molecule of Hg_2Cl_2...	$= 274,000$
Hence, total critical increment of reactants	$= 330,290$ cals.
Increment for one gram-molecule of $PbCl_2$ ...	$= 228,610$
,, ,, two gram-atoms of mercury ...	$= 124,870$
Hence, total critical increment of resultants	$= 353,480$ cals.

Hence, $Q = 353,480 - 330,290 = 23,190$ cals.

The value observed is 21,800 cals. approximately, Günther (*loc. cit.*). The agreement is satisfactory, especially as the critical increments are very large.

Silver Cyanide.

The heat of formation of this salt from silver and gaseous cyanogen, as determined by Thomsen, is 1393 cals. per gram-molecule. This quantity is so small that it would be impossible to calculate it with any degree of precision by the method employed in previous cases. In addition, the question of the critical frequency of cyanogen is in an involved state (compare Grotrian and Runge, *Physikal. Zeitsch.*, 1914, **15**, 545). We may use the available data to calculate the critical frequency of cyanogen.

Rubens and von Wartenberg (*loc. cit.*) have observed the infra-red band of silver cyanide at $\lambda_r = 93\,\mu$ approximately. That is, $v_r = 0.0323 \times 10^{14}$, and employing the square-root rule in conjunction with the normal molecular weight of the salt, as we have done in the case of the silver haloids, we obtain 15.86×10^{14} for the ultra-violet frequency, and $\lambda_v = 189\,\mu\mu$. Hence the critical increment per gram-molecule is 150,000 cals. The stoicheiometric equation considered is $Ag + CN = AgCN$. We have already seen that the increment of one gram-atom of silver is 91,010 cals. The heat of formation being 1393 cals., the total critical increment of the reactants is (150,000 − 1393) cals. On subtracting the value for one gram-atom of silver, we find that the critical increment of the cyanogen group is 57,600 cals., or for one gram-molecule of cyanogen the value is 115,200 cals. Hence the frequency is 12.2×10^{14} or $\lambda_v = 246\,\mu\mu$. The author is unaware whether any measurements have been carried out with

cyanogen in this region of the spectrum. In the process considered, the energy term, 115,200 cals., is that required to break the link between the two carbon atoms in the molecule $(CN)_2$, thereby giving rise to two nascent groups of monocyanogen. This is quite distinct from the mechanism involved in the dissociation of gaseous cyanogen into carbon and nitrogen, in which the carbon–nitrogen linking is broken. This would probably require a very different amount of energy.

Summary.

1. In spite of the fact that many of the available data are inaccurate and incomplete, the foregoing consideration of high-temperature reactions indicates that the radiation expression is borne out in a fairly satisfactory manner.

2. The following table contains the observed and calculated values of the heat effects in those cases in which the necessary data are available to permit of the complete calculation being carried out. For the reactions considered the heat effect is in all cases positive, that is, heat is evolved.

Reaction.	Heat effect per gram-atom of first reactant.	
	Q observed.	Q calculated.
$K + Cl \longrightarrow KCl$	$\begin{cases} 105,600 \\ 99,650 \end{cases}$	100,330
$K + Br \longrightarrow KBr$	98,810	96,940
$Na + Cl \longrightarrow NaCl$	97,800	97,290
$K + I \longrightarrow KI$	83,100	112,320 ?
$Ag + Cl \longrightarrow AgCl$	29,940	32,140
$Ag + Br \longrightarrow AgBr$	26,200	26,930
$Ag + I \longrightarrow AgI$	18,100	15,820
$Tl + Cl \longrightarrow TlCl$	48,600	47,780
$Tl + Br \longrightarrow TlBr$	44,800	40,080
$Tl + I \longrightarrow TlI$	33,200	28,550
$Pb + Cl_2 \longrightarrow PbCl_2$	85,570	77,660
$Hg + Cl_2 \longrightarrow HgCl_2$	53,900	59,000
$Hg + Cl \longrightarrow \frac{1}{2}Hg_2Cl_2$	31,300	26,500
$Pb + 2AgCl \longrightarrow PbCl_2 + 2Ag$	24,590	21,300
$Pb + Hg_2Cl_2 \longrightarrow PbCl_2 + 2Hg$	21,800	23,190

In a subsequent paper it is proposed to consider the data available in connexion with reactions which proceed at a sensible velocity at the ordinary temperature, that is, reactions which require quanta belonging to the short infra-red region to supply the energy necessary for the critical increments.

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The Relation Between Chemical Constitution and Physiological Action.

A Lecture delivered before the Chemical Society on December 6th, 1917.

By FRANK LEE PYMAN.

THE study of the relation between chemical constitution and physiological action is a branch of research which has a definite place in the investigation of medicinal substances. Chemical research on a drug begins with the attempt to isolate the principle to which its physiological action is due, and when this has proved successful the next step is the determination of the constitution of the active principle by analytic and synthetic methods. The knowledge is thus gained that some compound of known chemical structure has a particular physiological effect, and the way is then clear for the study of the relation between chemical constitution and physiological action by the preparation of a number of substances related to the parent compound and comparison of their actions on the living organism. The history of quinine affords an illustration of this sequence. Cinchona bark was employed as a remedy for malarial fevers in the fifteenth century. Later on, the alkaloid quinine was isolated, and recognised as the chief active principle of the drug. Chemical investigation eventually established the structure of the alkaloid, and attempts have since been made to improve, or vary, its medicinal properties by slight alterations of the molecular structure, such as reduction of the vinyl group and replacement of the methoxyl by higher alkyloxyl groups. Moreover, a number of compounds with the following general formula have been synthesised, which,

$$CH(OH)\cdot CH_2\cdot NRR'$$
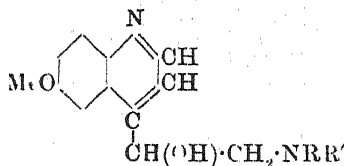
in common with quinine, are distinguished as powerful febrifuges combining a low toxicity to man and a high toxicity to infusoria and paramœcia.

The study of the relation between chemical constitution and physiological action may have various objects, philosophic or

practical. From the purely scientific point of view, it is of great interest to determine the change in physiological action resulting from modification of the chemical structure of an active compound and to elucidate the groups within its molecule to which its predominant physiological action is due; whilst, from the practical standpoint, the work may be directed to the physiological, chemical, or physical improvement of a drug—for instance, it may be desired to eliminate some undesirable secondary effect while maintaining the chief physiological action of the drug, or to prepare a derivative more stable or more soluble than the parent compound.

The relation between chemical constitution and physiological action has a significance in the discovery of new drugs similar to the relation between chemical constitution and colour in the discovery of new dyes. In the latter case, however, a single physical property, the absorption of light of different wave-lengths, is studied; whereas the term physiological action has no simple meaning, but covers any action on the living organism. The bactericidal action of phenol, the hypnotic properties of diethyl-barbituric acid, and the local anæsthetic action of cocaine are examples of physiological action which are no more comparable with one another than are the chemical structures of the three drugs. Moreover, it should be borne in mind that the same superficial signs of physiological action may be due to different causes. Purgation, for instance, is caused by saline cathartics, such as magnesium sulphate, which act by increasing the bulk of fluid in the intestines; and by vegetable purgatives, such as derivatives of anthraquinone, which act by irritating the epithelium of the intestines, thus promoting peristalsis. The difficulty of generalisation in the relation under discussion may be instanced by the effect of introducing a methyl group into the ortho-position of a phenol, where, in the case of the parent compound, the resulting o-cresol is a more powerful germicide than phenol, whilst a similar substitution in p-hydroxy-β-phenylethylamine leads to a substance, 4-hydroxy-β-m-tolylethylamine, which has only one-half of the pressor properties of the parent compound. The subject of this paper must therefore be subdivided eventually into a number of fragments on the relation between chemical constitution and a particular physiological effect; but before proceeding with these, some general remarks on the action of drugs may be made.

An example of physiological action which everyone can appreciate without special knowledge is the effect of certain volatile compounds on the terminations of the olfactory nerves, producing the sense of smell. Many compounds of similar constitution have

the same type of smell—for instance, the lower fatty acids, whilst each member may have a specific odour—which, in this particular case, serves to distinguish the individual members from formic to valeric acids.   Sense of taste also provides an occasional means of discrimination, not only between side chains of different lengths —*p*-ethoxyphenylcarbamide (dulcine) being sweet, whilst the higher alkylphenylcarbamides are not—but also in certain cases between stereoisomerides—*d*-histidine, for example, tasting sweet, whilst *l*-histidine is tasteless.   It is noteworthy that stereochemical influences often have profound effects on the physiological actions of quite different classes of compounds, particularly in actions on nerve-endings, as Cushny has pointed out (*Lancet*, September 9th, 1916, 459); thus, *l*-hyoscyamine has about 100 times the mydriatic action of the *d*-variety and *l*-adrenaline has many times the pressor effect of *d*-adrenaline.   In the case of pilocarpine, which contains two asymmetric carbon atoms, a change of sign of one of these results in the formation of the stereoisomeric *iso*pilocarpine, which has only a fraction of the activity of pilocarpine itself.   The asymmetry of a nitrogen atom may also condition a difference in physiological action; when *l*-canadine is methylated, a mixture of the α- and β-methochlorides is obtained, the isomerism of which is due to the asymmetry of the nitrogen atom; these produce a typical curare effect (paralysis of nerve endings in voluntary muscle) in the frog, the β-salt being, however, twelve times as powerful as the α-salt.   Stereoisomerides, however, do not always show large differences in physiological action, even in actions on nerve-endings; *d*- and *l*-homatropine differ little from each other and *dl*-homatropine in mydriatic action, whilst *d*-cocaine, a stereoisomeride of natural lævorotatory cocaine, has a local anæsthetic action which, although quicker and more intense, is also more evanescent than that of cocaine.

Very little is known about the cause of the variation in the physiological actions of stereoisomerides, but recently an explanation has been suggested by Windaus (*Nachr. K. Ges. Wiss. Göttingen*, 1916, 301) for the different physiological behaviour of the stereoisomerides β- and ε-cholestanol.   These compounds differ greatly in their power of inhibiting the hæmolytic action of saponins, such as digitonin, the former having this property in a high degree, whilst the latter has only slight preventive properties.   Now, the β-compound has been found to combine with digitonin to give an almost inactive additive product, whilst ε-cholestanol does not combine with digitonin.

This case is of special importance, because of the close relation of the cholestanols to cholesterol, a constituent of the living

organism; it may be that a similar difference in the ability of
stereoisomerides to combine with constituents of the nerve cells is
the cause of their different action in other cases also.

A point to be considered in connexion with the relation between
chemical constitution and physiological action is the effect of the
physical and chemical properties of the substance on its distribu-
tion in the organism. The influence of physical properties, such
as solubility in different media, may be of great importance, as
in the case of hypnotics, where Meyer and Overton found that the
narcotic effect of a series of aliphatic compounds on tadpoles was
proportional to the partition coefficients of their solubilities in oil
and water. An indication of the effect of chemical properties on
the distribution of drugs in the organism was afforded by the
work of Ehrlich (compare "v. Leyden-Festschrift," 1898). He
showed that basic dyes, such as methylene-blue, stained the grey
nerve substance, whereas their sulphonic acids did not, and this
difference suggested that bases, which are liberated in the blood-
stream by the alkali, are extracted by the nerve substances, whilst
their sulphonic acids remain in solution as alkali salts. Similarly,
the facility with which an alkaloid is extracted from aqueous
alkaline solutions by immiscible solvents may reasonably be sup-
posed to affect its distribution in the organism, and Ehrlich gave
examples of the change of action when certain basic drugs are
converted into derivatives containing a free acid grouping or into
quaternary salts.

In the case of alkaloids, it is a general rule that the introduc-
tion of a free carboxyl group into the molecule profoundly modifies
the physiological action of the parent compound. Benzoylecgonine,
of which cocaine is the methyl ester, has no local anæsthetic action;
quitenine, the acid obtained by oxidising the vinyl group of quinine
to a carboxyl group, is non-toxic, but regains its toxicity on
ethylation; the lactone pilocarpine becomes inactive on the addi-
tion of a molecule of alkali hydroxide, which forms the alkali salt
of the corresponding hydroxy-acid, whilst a similar loss of physio-
logical activity is shown by a series of tropeines containing a
lactone group, which lose their atropine-like action on the addition
of a molecule of alkali hydroxide.

The formation of quaternary salts likewise very largely affects
the physiological properties of alkaloids, and was the subject of
study many years ago by Crum-Brown and Fraser. To give an
example from more recent work, Laidlaw (*Biochem. J.*, 1910, **5**,
243) found that 6:7-dimethoxy-3:4-dihydro*iso*quinoline (I) had a
strychnine-like effect, whilst its methochloride (II) was devoid of

this property, which, however, reappeared in its reduction product
6 : 7-dimethoxy-2-methyltetrahydro*iso*quinoline (III).

(I.)   (II.)   (III.)
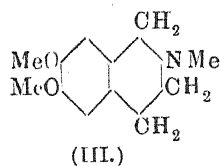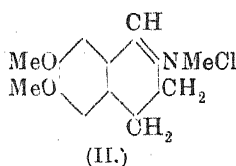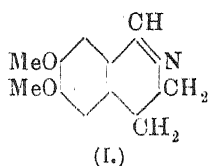
A similar relation was observed with papaverine (IV), its metho-
chloride (V), and the reduction product of the latter, laudanosine

(IV.)   (V.)

(VI.)
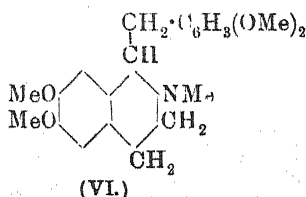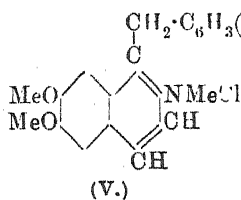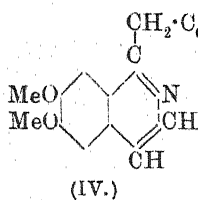
(VI); here also the tertiary bases were characterised by strychnine-
like action, which was not obtained with papaverine methochloride.

Having directed attention to the complication introduced into
the relation under discussion by the effect of physical and chemical
properties on the distribution of drugs, we may now consider certain
difficulties of generalisation.   We have seen that certain compounds
closely allied in chemical constitution differ remarkably in their
action, and we find, on the other hand, groups of substances which
are almost indistinguishable physiologically, but have little in
common from the point of view of chemical constitution ; one such
group is formed by the alkaloids nicotine, lobeline, and cytisine,
another by muscarine, arecoline, and pilocarpine.   Experience has
shown, however, that the members of a group of chemical com-
pounds of similar constitution often resemble one another in
physiological action, and in such cases it is of interest to observe
the effect of slight alterations in chemical structure.   Many such
investigations have been carried out, and will be known to you.
To-night I shall confine my attention to a few lines of work in

this field which have been carried out or materially advanced within the last ten years, selecting especially those with which the Wellcome Research Laboratories have been associated.

Tropeines.

The compounds known as tropeines are the acyl derivatives of the amino-alcohol tropine. Atropine, the parent member of the group, is the dl-tropyl ester of tropine, and readily yields this sub-

$$CH_2\!\!-\!\!CH\!\!-\!\!CH_2$$
$$| \quad\quad NMe \ \ CH{\cdot}O{\cdot}CO{\cdot}CHPh{\cdot}CH_2{\cdot}OH.$$
$$CH_2\!\!-\!\!CH\!\!-\!\!CH_2$$
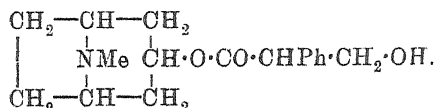
stance on hydrolysis. By esterifying tropine with other acids, tropeines containing different acyl groups may be prepared. A number of these have been examined physiologically, the best known being homatropine, the mandelyl ester of tropine, which was described by Ladenburg in 1883. In this paper I propose to give an account of the work on the relation between chemical constitution and physiological action in the tropeines, carried out some years ago by Dr. H. A. D. Jowett and myself with the co-operation of Dr. H. H. Dale, F.R.S. (*Seventh Internat. Congr. Appl. Chem.*, 1909, IVA, 1, 335), in continuation of an investigation commenced by Dr. Jowett in collaboration with Dr. C. R. Marshall.

The tropeines appeared to us to be specially suitable for a study of the relation between chemical constitution and physiological action, since they are easily prepared, give neutral salts readily soluble in water, and can be tested physiologically under uniform conditions. Their salts were dissolved in distilled water to give solutions equivalent in tropine content to a 1 per cent. solution of homatropine hydrobromide, and the mydriatic effects of these solutions were then compared.

By means of two pipettes delivering drops of equal size, a drop of one of the two solutions to be compared was allowed to fall into the right eye of a cat, and a drop of the other exactly at the same moment into the left eye, the head being held until all was absorbed, so that none escaped by overflow of tears. In the case of the less active tropeines, the times required to produce the maximum mydriatic effect were much the same in all cases, so that the more active of two was easily recognised. In the case of the highly active tropeines, the rapidity of action, as well as the maximum mydriatic effect, had to be considered.

It should be noted that the mydriasis caused by the more

powerful tends to produce consensual myosis in the other eye, so that a small difference of activity is exaggerated and easily detected.

The effect of concentrated solutions has not been tested, but tropeines which produce no perceptible effect in dilute solutions may give evidence of mydriatic effect when applied in concentrated form; thus Gottlieb (*Arch. exp. Path. Pharm.*, 1896, **37**, 218) has stated that lactyltropeine and hippuryltropeine produce no mydriasis when introduced into the conjunctival sac in 2 per cent. solution, but that 10 to 20 per cent. solutions produce mydriasis commencing in half an hour. Further, it must be pointed out that only the effect of *local* application has been tested; tropine itself, although it has no local action on the eye, produces a striking mydriasis in cats when given internally in large doses, and certain tropeines which have no local action, for example, the lactone of *o*-carboxyphenylglyceryltropeine, produce mydriasis on injection.

Briefly, the problem investigated was the relation between the chemical constitution of the acyl group of a tropeine and the mydriatic effect produced by the instillation of a neutral solution equivalent in tropine content to a 1 per cent. solution of homatropine hydrobromide into the conjunctival sac of a cat. No attempt was made to determine the cause of the mydriatic effect, which may have been due to action of the atropine type, that is, paralysis of the motor nerve-endings of the sphincter (contractor) muscle of the pupil, or to action of the cocaine type, that is, stimulation of the nerve-endings in the dilator muscle.

Thirty tropeines were prepared and examined comparatively by this method. The mydriatic action of many of these had been recorded previously, and references to the earlier results are given below. The mydriatic action of a further fifteen tropeines, which we ourselves did not examine, is also taken into consideration.

For the purpose of discussion, the forty-five tropeines may be divided conveniently into six groups.

I. Tropeines of aliphatic acids	8
II. Tropeines of substituted benzoic acids	6
III. Tropeines of substituted hydratropic acids	11
IV. Tropeines of substituted phenylacetic acids	13
V. Tropeines of substituted phenylpropionic acids	5
VI. Tropeines of acids in which the phenyl and carboxyl groups are separated by an imino-group	2

The tropeines of each group have been tabulated in order to show the results obtained at a glance.

I. *Tropeines of Aliphatic Acids.*

| Tropeine. | Formula. | Mydriatic action | | Present comparison. |
| | | Previous results | | |
		Action.	Observer.	Action.
1. Acetyl-	$CH_3 \cdot CO_2T$	—	Gottlieb	
2. Glycollyl-	$CH_2(OH) \cdot CO_2T$	—	Marshall[1]	
3. Lactyl-	$CH_3 \cdot CH(OH) \cdot CO_2T$	$\{ \begin{array}{l} -2\% \\ +10 \text{ to } 20\% \end{array}$	Gottlieb	
4. Succinyl-	$(\cdot CH_2 \cdot CO_2T)_2$	—	Gottlieb	
5. Tartryl-	$[\cdot CH(OH) \cdot CO_2T]_2$			—
6. Fumaroyl-	$(:CH \cdot CO_2T)_2$			—
7. Methylparaconyl-	$\begin{array}{c} CHMe \cdot CH \cdot CO_2T \\ \mid \qquad \mid \\ O \cdot CO \cdot CH_2 \end{array}$	—	Marshall[1]	—
8. Terebyl-	$\begin{array}{c} CMe_2 - CH \cdot CO_2T \\ \mid \qquad \mid \\ O \cdot CO \cdot CH_2 \end{array}$	+	Marshall[1]	—

[1] Jowett and Hann, T., 1906, **89**, 357.

Gottlieb stated that acetyl- and succinyl-tropeines can be brought in the solid state on to the conjunctival sac of a cat without perceptible mydriatic effect, but that lactyltropeine produces mydriasis commencing in half an hour under these conditions, although it is inactive when applied as a 2 per cent. solution.

The above table shows that previous observers had only reported mydriatic activity of dilute solutions in one instance, that of terebyltropeine. This compound was again examined in the course of the present work, and found to be inactive. Tartryl- and fumaroyl-tropeines were also inactive, so that no aliphatic tropeine that has yet been tested possesses mydriatic properties when applied as a dilute solution to the eyes of a cat.

II. *Tropeines of Substituted Benzoic Acids.*

| Tropeine. | Formula. | Mydriatic action. | | Present comparison. | |
| | | Previous results. | | | Order of activity. |
		Action.	Observer.	Action.	
9. Benzoyl-	$C_6H_5 \cdot CO_2T$	+	Schmiede-berg.[1]	+	3
10. Phthaloyl-	$C_6H_4(CO_2T)_2$				
11. o-Hydroxybenzoyl-	$HO \cdot C_6H_4 \cdot CO_2T$	—	Falck[2]	+	1
12. m-Hydroxybenzoyl-	$HO \cdot C_6H_4 \cdot CO_2T$	+	Völkers[2]	+	2
13. p-Hydroxybenzoyl-	$HO \cdot C_6H_4 \cdot CO_2T$			—	
14. Protocatechoyl-	$(HO)_2C_6H_3 \cdot CO_2T$	—	Marshall	—	

[1] R. Buchheim, *Arch. exp. Path. Pharm.*, 1876, **5**, 463.
[2] Ladenburg, *Annalen*, 1883, **217**, 82.

Our examination of the above tropeines confirmed the statements of previous observers, except in the case of *o*-hydroxybenzoyltropeine. So far from being inactive, this proved to be the most active of the tropeines of substituted benzoic acids, *m*-hydroxybenzoyltropeine being the next in order of activity. The tropeines of *p*- nd 3 : 4-dihydroxy-benzoic acids, both containing a para-hydroxyl group, were inactive.

III. *Tropeines of Substituted Hydratropic Acids.*

Tropeine.	Formula	Mydriatic action.			
		Previous results.		Present comparison.	
		Action.	Observer.	Action.	Degree.
15. *dl*-Tropyl-(atropine)	⎧ CH₂·OH	+	⎫ Cushny[1]	-|-	l
16. *l*-Tropyl-(hyoscyamine)	⎨	+	⎬ Laidlaw[2]		
17. *d*-Tropyl-(*d*-hyoscyamine)	⎩ CHPh·CO₂T	+	⎭		
18. Atropine methonitrate..	CH₂·OH	+	Erbe[3]		
	CHPh·CO₂T,MeNO₃		Grube[4]		
19. Acetyltropyl-	CH₂·O·CO·CH₃	+	Lewin and		
	CHPh·CO₂T		Guillery[5]		
20. Chlorohydratropyl-	CH₂Cl	-|-	Lewin and		
	CHPh·CO₂T		Guillery[5]		
21. Bromohydratropyl-	CH₂Br	+	Lewin and		
	CHPh·CO₂T		Guillery[5]		
22. Atropinesulphuric acid	CH₂·O·SO₃H	—	Trendel-		
	CHPh·CO₂T		enburg[6]		
23. Atroglyceryl-	CH₂·OH			+	2
	CPh(OH)·CO₂T				
24. Atrolactyl-	CPhMe(OH)·CO₂T	+	Völkers		
25. Atropyl-	CPh(:CH₂)·CO₂T	—	Lewin and		
			Guillery[5]		

[1] *J. physiol.*, 1904, **30**, 176.

[2] Barrowcliff and Tutin, T., 1909, **95**, 1906.

[3] *Inaug. Diss.*, München, 1903.

[4] *Inaug. Diss.*, Göttingen, 1905.

[5] " Die Wirkungen von Arzneimitteln und Giften auf das Auge," Berlin, 1905, p. 209.

[6] *Arch. exp. Path. Pharm.*, 1913, **73**, 118.

The tropeines of substituted hydratropic acids present several points of interest, the most striking being the difference in activity between *l*- and *d*-hyoscyamine. Cushny, working with the partly racemised substances, found that *l*-hyoscyamine was about fourteen

times as active a mydriatic as *d*-hyoscyamine. Later, Laidlaw showed that the ratio of activity between the pure salts was much greater, the mydriatic action of the *l*-compound being about one hundred times that of the dextro-compound. The mydriatic action of atropine is therefore mainly due to the *l*-constituent.

Methylation of the nitrogen atom of atropine decreases the mydriatic action, atropine methonitrate being apparently intermediate in action between atropine and homatropine.

Acetylatropine is stated by Lewin and Guillery to cause mydriasis and paralysis of the accommodation when applied in 1 per cent. solution, whilst the same authors report that chloro- and bromo-hydratropyltropeines in 2 per cent. solution cause greater irritation to the eyes than atropine. The chloro-compound, although less active than atropine, gives sufficient mydriasis for ophthalmic purposes, whilst the action of the bromo-compound is even slower and less intense than that of the chloro-compound. They found that atropyltropeine caused no mydriasis in 2 per cent. solution.

Atropinesulphuric acid, the acid sulphuric ester of atropine, and at the same time an internal salt, has no mydriatic action in 1 per cent. solution.

Atroglyceryltropeine is of particular interest, since it contains two hydroxyl groups in the positions of those of atropine and homatropine respectively.
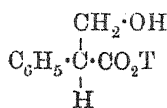
$$
\begin{array}{ccc}
\mathrm{CH_2 \cdot OH} & \mathrm{CH_2 \cdot OH} & \mathrm{H} \\
| & | & | \\
\mathrm{C_6H_5 \cdot \overset{|}{C} \cdot CO_2T} & \mathrm{C_6H_5 \cdot \overset{|}{C} \cdot CO_2T} & \mathrm{C_6H_5 \cdot \overset{|}{C} \cdot CO_2T.} \\
| & | & | \\
\mathrm{H} & \mathrm{OH} & \mathrm{OH} \\
\text{Atropine.} & \text{Atroglyceryltropeine.} & \text{Homatropine.}
\end{array}
$$
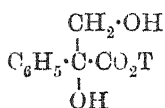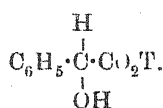
When examined on cats by the comparative method, it proved to be intermediate in activity between atropine and homatropine, but was less active than homatropine for the human eye. Atrolactyltropeine is described as a powerful mydriatic, strikingly similar in this respect to homatropine.

With the exception of homatropinesulphuric acid, which is inactive, like atropinesulphuric acid in the previous section, all the tropeines of substituted phenylacetic acids have mydriatic properties. The effect of stereoisomerism on the activity is much less marked than in the previous section, the enantiomorphous forms of homatropine differing only slightly in action, the lævo-form being again the more active.

Homatropine methobromide dilates the pupils of cats' eyes more completely and more quickly than a solution of homatropine

IV. *Tropeines of Substituted Phenylacetic Acids.*

| | | Mydriatic action. | | |
| | | Previous results. | | Present comparison. |
Tropeine.	Formula.	Action.	Observer.	Action.
26. Phenylacetyl- ...	$CH_2Ph \cdot CO_2T$			$+$
27. *dl*-Mandelyl- (homatropine)..		$+$	Völkers	$+$
28. *d*-Mandelyl-	$CHPh(OH) \cdot CO_2T$			$+$
29. *l*-Mandelyl-				$+$
30. *dl*-Mandelyl- methobromide	$CHPh(OH) \cdot CO_2T, MeBr$	$+$	Symons [1]	$+$
31. *dl*-Mandelyl-etho- bromide	$CHPh(OH) \cdot CO_2T, EtBr$	$+$	Symons [1]	$+$
32. Homatropine-sul- phuric acid......	$CHPh(O \cdot SO_3H) \cdot CO_2T$	$-$	Trendel- enburg	
33. *o*-Methylmandelyl-				$+$
34. *m*-Methylmandelyl-	$C_6H_4Me \cdot CH(OH) \cdot CO_2T$			$+$
35. *p*-Methylmandelyl-				$+$
36. Phenylchloro- acetyl-	$CHPhCl \cdot CO_2T$			$+$
37. Phenylamino- acetyl-	$CHPh(NH_2) \cdot CO_2T$			$+$
38. Phthalidecarboxyl-	$C_6H_4 \cdot CH \cdot CO_2T$ $\|$ $CO — O$	$+$	Marshall	$+$

[1] Jowett and Pyman, T., 1907, **91**, 92.

hydrobromide of the same strength, but is less active for human eyes. Homatropine ethobromide is less active than the metho-bromide. Of the three methylmandelyltropeines, the ortho- and meta-compounds equal each other and are more powerful than homatropine in mydriatic power when tested on cats, but the para-compound is slightly less active.

Phenylacetyl-, phenylchloroacetyl-, phenylaminoacetyl-, and phthalidecarboxyl-tropeines, which contain no free alcoholic hydroxyl group, are all active, but much less so than homatropine.

Cinnamoyltropeine, reported by Ladenburg as "hardly mydriatic," was found to have no mydriatic properties under the conditions of our investigation. β-Phenyl-α-hydroxypropionyl-tropeine is isomeric with atropine (α-phenyl-β-hydroxypropionyl-tropeine) and also with atrolactyltropeine (α-phenyl-α-hydroxy-propionyltropeine); it only differs from homatropine in that the phenyl and secondary alcohol groups are separated by a methylene group. It is a powerful mydriatic for cats' eyes, and begins to dilate the pupil considerably earlier than atropine, but the atropine dilation when it once begins quickly overtakes the other

V. *Tropeines of Substituted Phenylpropionic Acids.*

Tropeine.	Formula.	Mydriatic action.			
		Previous results.		Present comparison.	
		Action.	Observer.	Action.	Degree.
39. Cinnamoyl-	CHPh:CH·CO$_2$T	—	Ladenburg	—	
40. Lactone of o-carb-oxyphenyl-glyceryl-	C$_6$H$_4$·CH(OH)·CH·CO$_2$T | | CO————O	—	Symons	—	
41. isoCoumarincarb-oxyl-	C$_6$H$_4$·CH:C·CO$_2$T | | CO————O	—	Symons	—	
42. β-Phenyl-α-hydr-oxypropionyl-	CH$_2$Ph·CH(OH)·CO$_2$T			+	1
43. β-2-Pyridyl-α-hydroxypro-pionyl-	C$_5$H$_4$N·CH$_2$·CH(OH)·CO$_2$T			+	2

and becomes maximal a little earlier. When tested on human eyes, it was found to be inferior to homatropine hydrobromide.

β-2-Pyridyl-α-hydroxypropionyltropeine has been included in the above group. It differs from the preceding member by the substitution of pyridine for benzene, and, although active, is considerably weaker.

VI. *Tropeines of Acids in which the Phenyl and Carboxyl Groups are Separated by an Imino-group.*

Tropeine.	Formula.	Mydriatic action.		Present comparison.
		Previous results.		
		Action.	Observer.	Action.
44. Hippuryl-	C$_6$H$_5$·CO·NH·CH$_2$·CO$_2$T	$\begin{cases} -2\% \\ +10 \text{ to } 20\% \end{cases}$	Gottlieb	
45. Phenylcarb-amo-	C$_6$H$_5$·NH·CO$_2$T			+

Gottlieb states that hippuryltropeine behaves similarly to lactyltropeine, that is to say, it only exercises a mydriatic effect when the solid substance is introduced into the conjunctival sac to give a concentrated solution, and is inactive in dilute solution. Phenylcarbamotropeine proved to have a slight mydriatic action.

In the foregoing tables, the tropeines are classified according to

their chemical constitution. The thirty members which we com-
pared by the method given above may be grouped also in order of
their mydriatic properties.

I. Atropine
    β-Phenyl-α-hydroxypropionyl-   } Most active.
        tropeine

II. Atroglyceryltropeine   Intermediate in activity be-
                                            tween atropine and hom-
                                            atropine.

III. *dl*-Homatropine
      d- and *l*-Homatropine   } Of a similar order of activity.
      Quaternary salts of homatropine
      o-, *m*-, and *p*-Methylhomatropine

IV. β-2-Pyridyl-α-hydroxypropionyl-
        tropeine
     Phthalidecarboxyltropeine
     Phenylchloroacetyltropeine
     Phenylaminoacetyltropeine   } All active, but less so than
     Phenylacetyltropeine   homatropine.
     Benzoyltropeine
     o-Hydroxybenzoyltropeine
     m-Hydroxybenzoyltropeine

V. Phenylcarbamotropeine   Faintly active.

VI. Tartryltropeine
     Fumaroyltropeine
     Methylparaconyltropeine
     Terebyltropeine
     Lactone of *o*-carboxyphenylglyceryl-
        tropeine   } Inactive.
     *iso*Coumarincarboxyltropeine
     Phthaloyltropeine.
     p-Hydroxybenzoyltropeine
     Protocatechoyltropeine
     Cinnamoyltropeine

Of the fifteen tropeines which we did not examine by the com-
parative method, natural hyoscyamine, which is the lævo-variety,
is nearly twice as active as atropine, *d*-hyoscyamine much less
so. Acetylatropine, chlorohydratropyltropeine, bromohydratropyl-
tropeine, atrolactyltropeine, and atropine methonitrate appear
to be equivalent in mydriatic power to the members of groups II
and III of the above table, whilst the following are stated to be
inactive in dilute solution:

Acetyltropeine.   Atropyltropeine.
Glycollyltropeine.   Hippuryltropeine.
Lactyltropeine.   Atropinesulphuric acid.
Succinyltropeine.   Homatropinesulphuric acid.

Before considering whether any general conclusions can be
drawn from these results, attention may be directed to the general-
isation which has found its way into the literature, sometimes in

association with Ladenburg's name.   This generalisation states that a tropeine to have mydriatic properties must contain (1) a benzene nucleus, and (2) an alcoholic hydroxyl group in the side chain containing the carboxyl group.

Now Ladenburg stated in 1883 that m-hydroxybenzoyltropeine had mydriatic properties, so it seemed unlikely that the generalisation was due to him. Accordingly, after a careful but unsuccessful search of the literature for such a generalisation under Professor Ladenburg's name, we communicated with him, and learned that he was unable to recollect framing it.

In the light of the evidence afforded above, it would appear that the first postulate of this generalisation is approximately correct; no tropeine of an aliphatic acid has yet been found to possess mydriatic properties in dilute solution, but, on the other hand, the closed chain need not necessarily be that of benzene, since β-2-pyridyl-α-hydroxypropionyltropeine, which contains a pyridine instead of a benzene residue, is active.

The second postulate, that a tropeine to be mydriatic must have an alcoholic hydroxyl group in the side chain containing the carboxyl group, is incorrect, for mydriatic substances are obtained when the hydroxyl group of atropine is exchanged for acetoxyl, chlorine, or bromine, and when the hydroxyl group of homatropine is exchanged for hydrogen, chlorine, or an amino-group, or when it is closed by the formation of a lactone; moreover, benzoyl- and o- and m-hydroxybenzoyl-tropeines are mydriatic.   The loss of mydriatic properties on the replacement of the hydroxyl group in atropine and homatropine by the sulphuric acid residue is possibly due to the same cause which operates in the case of substances containing a free carboxyl group, such as benzoylecgonine and quitenine.

Whilst, however, the second postulate is incorrect as regards the qualitative mydriatic action of tropeines, it must be remembered that those tropeines which we found more active than, or equal to, homatropine in mydriatic properties contained an alcoholic hydroxyl group.

Of the tropeines of hydroxybenzoic acids, the o- and m-substituted compounds were active, whilst the p- and also the 3 : 4-dihydroxy-compounds were inactive.   Substitution in the p-position in this case causes the mydriatic action to vanish, and in the case of the methylmandelyltropeines also the para-compound is less active than the ortho- and meta-isomerides.

The tropeines of substituted hydratropic, phenylacetic, and phenylpropionic acids were all active with the exception of atropinesulphuric acid, homatropinesulphuric acid, the lactone of

o-carboxyphenylglyceryltropeine, and those containing an unsaturated linking in the side-chain containing the carboxyl group.

Consideration of the above material led us to conclude that no generalisation as to the relation between mydriatic action and chemical constitution could be made which would offer a strict explanation of the results obtained.

Before leaving the subject of the tropeines, attention may be directed to some points of interest in connexion with allied mydriatics. Norhyoscyamine, which differs from hyoscyamine in containing an imino- in the place of an *N*-methyl group, has only one-eighth of the mydriatic effect of hyoscyamine, and the racemic form, noratropine, is again about one-eighth as active as atropine (Carr and Reynolds, T., 1912, **101**, 946. Physiological tests by Laidlaw).

It has already been pointed out that the steric structure of the acyl radicle of a tropeine influences its mydriatic properties. The steric structure of the basic portion of the molecule is also important, for the tropyl and mandelyl esters of ψ-tropine have no mydriatic properties (Liebermann and Limpach, *Ber.*, 1892, **25**, 933. Physiological tests by Liebreich).

Aminoalkyl Esters.

The question as to what portions of the cocaine molecule (I) are essential to the local anæsthetic action of the alkaloid has long been the subject of investigation, and the collated results of numerous workers have shown, by a series of eliminations, that the anæsthetic properties of cocaine are associated with its function as an aminoalkyl ester. It has been found that the carboxymethyl (CO_2Me) group is not an essential factor, since tropa-—cocaine (II), which contains no such group, produces the same effect; and, further, the presence of a bridged or simple ring containing nitrogen is unnecessary, since eucaine (III), which possesses only a simple, not a bridged ring, and stovaine (IV), alypine (V), and novocaine (VI), which contain no such ring, have well-marked local anæsthetic properties.

$$CH_2 \cdot CH \!-\! CH \cdot CO_2Me$$
$$| \qquad NMe \quad CH \cdot O \cdot COPh$$
$$CH_2 \cdot CH \!-\! CH_2$$
(I.)

$$CH_2 \cdot CH \!-\! CH_2$$
$$| \qquad NMe \quad CH \cdot O \cdot COPh$$
$$CH_2 \cdot CH \!-\! CH_2$$
(II.)

$$CH_3 \cdot CMe \!-\! CH_2$$
$$| \qquad NH \quad CH \cdot O \cdot COPh$$
$$CH_3 \cdot CH \!-\! CH_2$$
(III.)

$$CH_2 \cdot NMe_2$$
$$C_2H_5 \cdot C \cdot O \cdot COPh$$
$$CH_3$$
(IV.)

$$\underset{\substack{| \\ \mathrm{CH_2 \cdot NMe_2}}}{\overset{\substack{\mathrm{CH_2 \cdot NMe_2} \\ |}}{\mathrm{C_2H_5 \cdot \overset{|}{C} \cdot O \cdot COPh}}} \qquad \mathrm{(C_2H_5)_2N \cdot CH_2 \cdot CH_2 \cdot O \cdot CO \cdot C_6H_4 \cdot NH_2}\ (p)$$

$$\text{(V.)} \qquad\qquad\qquad \text{(VI.)}$$
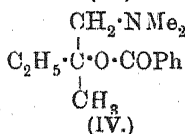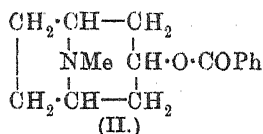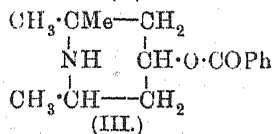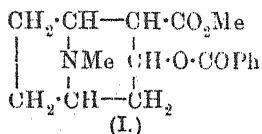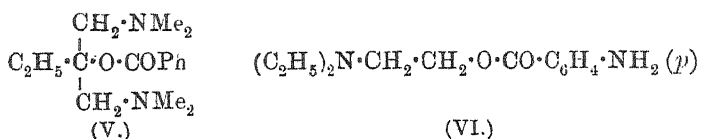
From the above considerations, it follows that local anæsthetic action is associated with the aminoalkyl ester structure, and we may now inquire what complexes in such esters are necessary for the possession of local anæsthetic properties. Aminoalkyl esters have the general formula $R \cdot CO \cdot O-(CR_1R_2)_x-NR_3R_4$; they are formed by the esterification of an *acid* with an *alcohol* containing an *amino*-group, and may be dealt with conveniently from this point of view.

The *acyl* group of aminoalkyl esters possessing local anæsthetic properties is in most cases aromatic, and in the majority of substances of practical application is the benzoyl group, as instanced by the compounds numbered I to V. Fourneau (*J. Pharm. Chim.*, 1910, [vii], **2**, 337, 397) has, however, recorded that the valeryl, bromovaleryl, and bromoheptoyl esters of dimethylaminodimethylethylcarbinol (the benzoate of which is stovaine) have anæsthetic properties, so that the presence of a ring complex in the acid does not appear to be essential.

In the case of cocaine, replacement of the benzoyl by substituted benzoyl or other acid radicles leads to substances with much weaker local anæsthetic properties. Thus the phenylacetyl derivative is much less powerful, the o-chlorobenzoyl and *m*-nitrobenzoyl derivatives have only a slight local anæsthetic action, and the *m*-hydroxybenzoyl compound still less, whilst the substances in which the benzoyl is replaced by the valeryl, *m*-aminobenzoyl, phthaloyl, cinnamoyl, or isatropyl radicles are inactive (Ehrlich, Liebreich, and Poulsson. Compare Ehrlich and Einhorn, *Ber.*, 1894, **27**, 1870). Substitution in the benzoic acid nucleus of aminoalkyl benzoates is not, however, necessarily associated with weak local anæsthetic action, for the p-aminobenzoyl esters of many amino-alcohols are strong local anæsthetics, novocaine being diethylaminoethyl p-aminobenzoate, whilst the dialkylaminoalkyl 3:4-diaminobenzoates have also considerable local anæsthetic properties (Einhorn, D.R.-P., 194365). In the case of cocaine, the substitution of phthaloyl for benzoyl gave an inactive compound, and, similarly, whilst diethylaminoethyl benzoate, $\mathrm{NEt_2 \cdot CH_2 \cdot CH_2 \cdot O \cdot COPh}$, is stated to have local anæsthetic properties (E. Schering, D.R.-P., 175080), diethylaminoethyl phthalate proved to be inactive (Pyman, T., 1908, **93**, 1793. Physiological

tests by Dale and Symons). Passing now to aromatic acids, in which the carboxyl of the acyl group is not directly attached to the benzene nucleus, we have seen that the replacement of the benzoyl by the phenylacetyl group in cocaine gives a substance having local anæsthetic properties; with α-eucaine, also, the phenylacetyl compound has well-marked local anæsthetic properties (Vinci, *Virch. Arch.*, 1898, **154**, 549); it was found, however, that replacement of the *p*-aminobenzoyl group by the *p*-aminophenylacetyl group in novocaine and anæsthesine (ethyl *p*-aminobenzoate) gave inactive compounds, diethylaminoethyl and ethyl *p*-aminophenylacetates (Pyman, this vol., p. 167. Physiological tests by Dale and Symons).

Cinnamic acid usually, but not invariably, confers local anæsthetic properties on aminoalkyl esters. As we have seen, cinnamoylcocaine is inactive, but the α-eucaine derivative has local anæsthetic properties (Vinci, *loc. cit.*). Tetramethyldiaminodimethylethylcarbinyl cinnamate, that is, an " alypine " in which cinnamic acid takes the place of benzoic acid, produces an anæsthetic effect lasting twice as long as that brought about by the same quantity of cocaine (Farbenfabriken vorm. F. Bayer & Co., D.R.-P., 173631), whilst γ-diethylaminopropyl cinnamate (apothesine) also has well-marked local anæsthetic properties (E. A. Wildman and L. Thorp, U.S. Pat., 1193649).

It may be noted that the aminoalkyl esters of aminocinnamic acid are stated to have several times the local anæsthetic power of those of aminobenzoic acid (Meister, Lucius, & Brüning, D.R.-P., 187593).

With regard to the nature of the substituted *amino*-group required in an alkamine ester having local anæsthetic properties, there is little available information. Most of the best known local anæsthetics contain a tertiary amino-group, but β-eucaine, which has powerful local anæsthetic properties, contains a secondary amino-group. Norcocaine, in which the *N*-methyl group is replaced by the imino-group, has greater local anæsthetic properties than cocaine (compare Ehrlich and Einhorn, *loc. cit.*), but the primary amine corresponding with novocaine, namely, β-aminoethyl *p*-aminobenzoate (VII) (Forster, T., 1908, **93**, 1865. Physiological tests by Dale), is devoid of local anæsthetic action.

The nature of the alkyl groups replacing the hydrogen atoms of the amino-group appears to affect the local anæsthetic properties in some degree; thus, piperidylethyl benzoate (VIII) is only slightly active, whilst *s*-di-β-benzoyloxy-1:4-diethylpiperazine (IX) has very distinct action, and ββ-dibenzoyloxytriethylamine (X) is

slightly active, whilst $\beta\beta$-dibenzoyloxymethyldiethylamine (XI) (Pyman, *loc. cit.*) is inactive.

$$NH_2 \cdot CH_2 \cdot CH_2 \cdot O \cdot CO \cdot C_6H_4 \cdot NH_2 \qquad\qquad C_5H_{10}N \cdot CH_2 \cdot CH_2 \cdot O \cdot COPh$$
$$\text{(VII.)} \qquad\qquad\qquad\qquad\qquad \text{(VIII.)}$$

$$PhCO \cdot O \cdot CH_2 \cdot CH_2 \cdot N \!\!<^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}\!\!> N \cdot CH_2 \cdot CH_2 \cdot O \cdot COPh$$
$$\text{(IX.)}$$

$$NEt(CH_2 \cdot CH_2 \cdot O \cdot COPh)_2 \qquad\qquad NMe(CH_2 \cdot CH_2 \cdot O \cdot COPh)_2$$
$$\text{(X.)} \qquad\qquad\qquad\qquad\qquad\qquad \text{(XI.)}$$
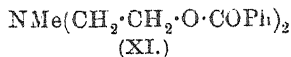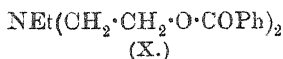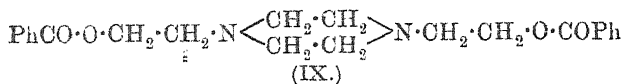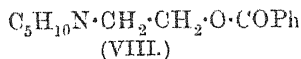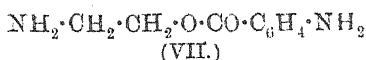
The *alcohol* residues of these esters are very varied in character; they may be primary, secondary, or tertiary, and may separate the acyl residue and the substituted amino-group by chains of a varying number of carbon atoms.

As instances of active aminoalkyl esters derived from primary alcohols, we have novocaine and the dialkylaminoethyl benzoates; in these, only two carbon atoms separate the acyl- and amino-groups. γ-Diethylaminopropyl cinnamate is an example of an ester of a primary alcohol in which the two groups referred to are separated by three carbon atoms. Cocaine, tropacocaine, and the eucaines are derived from secondary alcohols containing a chain of three carbon atoms between the acyl- and amino-groups, whilst instances of local anæsthetic property in secondary alcohols, in which these groups are separated by only two carbon atoms, are furnished by β-benzoyloxy-β-3:4-methylenedioxyphenylethyldimethylamine (I) and $\beta\gamma$-dibenzoyloxydimethylpropylamine (II) (Pyman, *loc. cit.*).
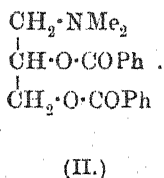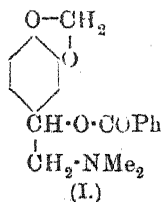
Finally, typical examples of local anæsthetics derived from tertiary alcohols are stovaine and alypine, in which the acyl and amino-groups are also separated by a chain of two carbon atoms.

The general conclusions to be drawn from the above summary are that in aminoalkyl esters having local anæsthetic properties (1) the acyl group is usually aromatic, (2) the amino-group may be secondary or tertiary, and may be associated with simple or bridged ring complexes, and (3) the alcohol group may be primary,

secondary, or tertiary, and may separate the acyl and amino-groups by a chain of either two or three carbon atoms.

Adrenaline and the Amines.

Adrenaline, the active principle of the suprarenal gland, is a substance of powerful physiological action. Its action simulates the effects of exciting sympathetic nerves, and in consequence has been termed "sympathomimetic."

Therapeutically, it is chiefly used to prevent bleeding by its vasoconstrictor action when applied locally; when injected intravenously, it causes, amongst other symptoms, a large rise of blood pressure, also partly due to vasoconstriction, and the measure of this pressor effect, when accompanied by other symptoms of sympathomimetic action, serves for the comparison of adrenaline with allied compounds.

Adrenaline is of comparatively simple constitution, being β-3:4-trihydroxy-β-phenylethylmethylamine (I), and the question as to the relative influences of the different portions of its molecular structure has been the subject of much investigation. It was at one time suggested that the catechol nucleus (II) was the essential active group, for catechol causes a rise of blood pressure on intravenous injection, whilst the other half of the molecule, β-hydroxyethylmethylamine (III), has no such action.

OH
OH
CH·OH
CH₂·NHMe
(I.)

OH
OH
(II.)

CH₂·OH
CH₂·NHMe
(III.)
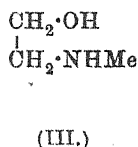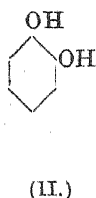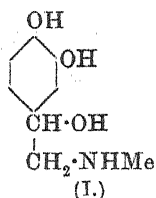
Barger and Dale (*J. Physiol.*, 1910, **41**, 19), however, showed that the rise of blood pressure produced by catechol was not due to sympathomimetic action, but to an action of an entirely different type, whilst, on the other hand, many aliphatic and aromatic amines had an action very similar to that of adrenaline. They studied the relation between chemical constitution and sympathomimetic action in a large number of amines gradually approaching adrenaline in constitution, and as a quantitative index of the activity of the compounds they adopted the effect on arterial blood pressure. The aliphatic amines were first examined, then those containing a phenyl group, and finally phenylalkylamines, in which one, two, or three hydroxyl groups were introduced as substituents into the benzene nucleus. In the aliphatic series, the following

results were obtained with primary amines under comparable conditions:

Substance.	Pressor effect.
(1) Methylamine	
(2) Ethylamine	
(3) isoPropylamine	insignificant.
(4) n-Propylamine	
(5) isoButylamine	
(6) n-Butylamine,	positive.
(7) isoAmylamine,	several times that of No. 6.
(8) n-Amylamine,	distinctly greater than that of No. 7.
(9) n-Hexylamine,	greater than that of No. 8.
(10) n-Heptylamine,	less than that of No. 9.
(11) n-Octylamine,	less than that of No. 10.

With still higher members of the series, comparison was difficult, since they became increasingly toxic.

Of secondary amines, diethylamine was found to be inactive, methylisoamylamine, C_5H_{11}·NHMe, was considerably weaker than isoamylamine, whilst diisoamylamine had very little of the action. In the aliphatic series, therefore, the most active member proved to be n-hexylamine.

The next group examined consisted of aromatic amines in which the benzene nucleus was otherwise unsubstituted.

(1) Aniline,	Ph·NH$_2$,	did not show the specific action.
(2) Benzylamine,	Ph·CH$_2$·NH$_2$,	had a mere trace of the action.
(3) α-Phenylethylamine,	Ph·CHMe·NH$_2$,	was very feebly active.
(4) β-Phenylethylamine,	Ph·CH$_2$·CH$_2$·NH$_2$,	was more active than Nos. (3) and (5), and its activity was distinctly greater than that of n-hexylamine, the most active of the aliphatic amines.
(5) γ-Phenylpropylamine,	Ph·[CH$_2$]$_3$·NH$_2$,	was much less active than No. (4).

β-Phenylethylamine, which proved to be the most active of this series, contains the skeleton of adrenaline, but differs from it in lacking (1) the 3:4-dihydroxyl substituents of the benzene nucleus, (2) the hydroxyl substituent of the β-carbon atom, and (3) the methyl group attached to the nitrogen atom. The effect of the two last substitutions singly or together on β-phenylethylamine was tested by the examination of β-hydroxy-β-phenylethylamine, Ph·CH(OH)·CH$_2$·NH$_2$, β-phenylethylmethylamine,

$$\text{Ph·CH}_2\text{·CH}_2\text{·NHMe,}$$

and β-hydroxy-β-phenylethylmethylamine,

$$\text{Ph·CH(OH)·CH}_2\text{·NHMe,}$$

none of which differed noticeably in activity from β-phenylethylamine.

Further work was directed to determining the influence of phenolic hydroxyl groups on the action of these phenylalkyl-

amines, and in the first place the effect of introducing a single hydroxyl group was ascertained, with the following results:

(1) *p*-Hydroxy-β-phenylethylamine, $HO \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NH_2$.

3 to 5 times as active as β-phenylethylamine. Had about 1-20th of the activity of adrenaline.

(2) *m*-Hydroxy-β-phenylethylamine,

Equal to (1).

(3) *o*-Hydroxy-β-phenylethylamine,

No more active than β-phenylethylamine.

(4) 4-Hydroxy-β-*m*-tolylethylamine,

Half as active as (1).

Me

$HO \langle \quad \rangle CH_2 \cdot CH_2 \cdot NH_2$.

(5) β-*p*-Dihydroxy-β-phenylethylamine, $HO \cdot C_6H_4 \cdot CH(OH) \cdot CH_2 \cdot NH_2$.

Less active than (1).

(6) *p*-Hydroxy-ω-aminoacetophenone, $HO \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot NH_2$.

Feebly: about 1-10th as active as (1).

(7) *p*-Hydroxy-β-phenylethylmethylamine, $HO \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NHMe$.

About the same as (1).

(8) *p*-Hydroxy-β-phenylethylethylamine, $HO \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NHEt$.

Considerably less active than (1) and (7).

(9) *p*-Hydroxy-β-phenylethyldimethylamine, $HO \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NMe_2$.

Very much less active than (1) and (7).

(10) *p*-Hydroxy-β-phenylethyltrimethyl ammonium iodide, $HO \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NMe_3I$.

Action entirely different from that of adrenaline, resembling that of nicotine.

(11) *dl*-*p*-Hydroxy-α-phenylethylamine, $HO \cdot C_6H_4 \cdot CHMe \cdot NH_2$.

Very slightly active.

12) *l*-*p*-Hydroxy-α-phenylethylamine,

Very slightly active; not different from (11).

(13) *p*-Hydroxyphenylethylacetamide, $HO \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NHAc$.

Inactive.

(14) Tyrosine ethyl ester, $HO \cdot C_6H_4 \cdot CH_2 \cdot CH(CO_2Et) \cdot NH_2$.

Inactive.

The foregoing results show that the introduction of a hydroxyl group into phenylethylamine is accompanied by an increase in activity in the case of the *p*- and *m*-compounds, but not in that of the *o*-substituted compound.

Here again, as in the unsubstituted phenyl series, neither the introduction of a hydroxyl group in the β-position (5), nor methylation of the nitrogen (7) increases the activity of the parent compound, whilst the introduction of a larger alkyl group (8) or second methyl group (9) on the nitrogen atom seriously diminishes the activity of the compound.

The next group of compounds examined contained two phenolic hydroxyl groups, and included (*a*) derivatives of acetocatechol, (*b*) derivatives of ethylcatechol, and (*c*) derivatives of hydroxyethylcatechol. By determining the doses which produced rises of blood pressure to equal submaximal heights, the approximate average activity values were found to be as follows:

(a) (1) 3 : 4-Dihydroxy-ω-aminoacetophenone,

   (OH)$_2$C$_6$H$_3$·CO·CH$_2$·NH$_2$ .... 1·5

   (2) 3 : 4-Dihydroxy-ω-methylaminoacetophenone,

   (OH)$_2$C$_6$H$_3$·CO·CH$_2$·NHMe

   Weaker than No. (1); greater than No. (4).

   (3) 3 : 4-Dihydroxy-ω-ethylaminoacetophenone,

   (OH)$_2$C$_6$H$_3$·CO·CH$_2$·NHEt .... 2·25

   (4) 3 : 4-Dihydroxy-ω-propylaminoacetophenone,

   (OH)$_2$C$_6$H$_3$·CO·CH$_2$·NHPr .... 0·25

(b) (5) 3 : 4-Dihydroxy-β-phenylethylamine,

   (OH)$_2$C$_6$H$_3$·CH$_2$·CH$_2$·NH$_2$ 1

   (6) 3 : 4-Dihydroxy-β-phenylethylmethylamine,

   (OH)$_2$C$_6$H$_3$·CH$_2$·CH$_2$·NHMe 5

   (7) 3 : 4-Dihydroxy-β-phenylethylethylamine,

   (OH)$_2$C$_6$H$_3$ CH$_2$·CH$_2$·NHEt .... 1·5

   (8) 3 : 4-Dihydroxy-β-phenylethylpropylamine,

   (OH)$_2$C$_6$H$_3$·CH$_2$·CH$_2$·NHPr .... 0·25

(c) (9) dl-β-3 : 4-Trihydroxy-β-phenylethylamine,

   (OH)$_2$C$_6$H$_3$·CH(OH)·CH$_2$·NH$_2$ 50

   (10) dl-β-3 : 4-Trihydroxy-β-phenylethylmethylamine (dl-adrenaline), (OH)$_2$C$_6$H$_3$·CH(OH)·CH$_2$·NHMe........................ 35

   (11) l-β-3 : 4-Trihydroxy-β-phenylethylmethylamine (l-adrenaline) 50

In these series, the N-propyl derivatives were much less active than the N-methyl and N-ethyl derivatives, but there is no consistency in the relative values of the amino-, N-methyl, and N-ethyl derivatives; in the (a) series the N-ethyl, in the (b) series the N-methyl, and in the (c) series the amino-compound, was the most active of those examined.

Two amines containing three phenolic hydroxyl groups were also examined, namely, 2 : 3 : 4-trihydroxy-ω-aminoacetophenone,

$$(OH)_3C_6H_2·CO·CH_2·NH_2,$$
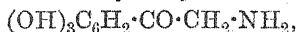
and 2 : 3 : 4-trihydroxy-β-phenylethylamine,

$$(OH)_3C_6H_2·CH_2·CH_2·NH_2.$$
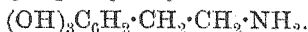
In each case the pressor action was somewhat weaker than that of the corresponding catechol base.

Consideration of the above results led Barger and Dale to the following conclusions: "The optimum carbon-skeleton for sympathomimetic activity consists of a benzene ring with a side-chain of two carbon atoms, the terminal one bearing the amino-group. Another optimum condition is the presence of two phenolic hydroxyls in the 3 : 4-position relative to the side-chain; when these are present, an alcoholic hydroxyl still further intensifies the activity. A phenolic hydroxyl in the ortho-position does not increase the activity.

Many physiologically active amines occur in nature as the result of decarboxylation of amino-acids by bacteria. Of those men-

tioned above, for instance, *iso*amylamine and *p*-hydroxy-β-phenyl-ethylamine are derived from leucine and tyrosine respectively.

$$HO \cdot C_6H_4 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H \longrightarrow HO \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NH_2.$$

Tyrosine.   *p*-Hydroxy-β-phenylethylamine.
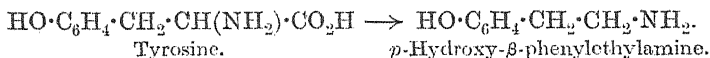
Derivatives of ethylamine containing heterocyclic nuclei are formed similarly, thus indole-ethylamine from tryptophan and aminoethylglyoxaline from histidine. Aminoethylglyoxaline occurs naturally in ergot, and is an intense stimulant of plain muscle; several of its derivatives and allied compounds listed below have been prepared and compared with it physiologically (Ewins, T., 1911, **99**, 2052; Pyman, *ibid.*, 2172; 1916, **109**, 186. Physiological tests by Laidlaw and Dale):

(1) 4-Aminomethylglyoxaline........................ $C_3H_3N_2 \cdot CH_2 \cdot NH_2$.
(2) 5-Methyl-4-aminomethylglyoxaline........... $Me \cdot C_3H_2N_2 \cdot CH_2 \cdot NH_2$.
(3) 5-Methyl-4-methylaminomethylglyoxaline $Me \cdot C_3H_2N_2 \cdot CH_2 \cdot NHMe$.
(4) 4-β-Aminoethylglyoxaline .... $C_3H_3N_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$.
(5) βγ-bis(4-Glyoxaline)-propylamine ....$\begin{cases} C_3H_3N_2 \cdot CH_2 \cdot \\ | \\ C_3H_3N_2 \cdot CH \cdot CH_2 \cdot NH_2. \end{cases}$
(6) β-Hydroxy-β-glyoxaline-4-ethylamine ...... $C_3H_3N_2 \cdot CH(OH) \cdot CH_2 \cdot NH_2$.
(7) 5-Methyl-4-aminoethylglyoxaline .... $Me \cdot C_3H_2N_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$.
(8) 1-Methyl-4-aminoethylglyoxaline .... $Me \cdot C_3H_2N_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$.
(9) 1-Methyl-5-aminoethylglyoxaline .... $Me \cdot C_3H_2N_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$.
(10) 4-γ-Aminobutylglyoxaline ....$C_3H_3N_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot NH_2$

Of these compounds, No. 6 was found to be less active than aminoethylglyoxaline (No. 4), and No. 7 had only about a 1/200th of the characteristic stimulant action of No. 4, whilst the remaining members of the series only showed this action to a slight extent. Here also the optimum side-chain has two carbon atoms between the cyclic system and the amino-group, the compounds in which one (No. 1) and three (No. 10) carbon atoms separated these groups being much less active. The introduction of an alcoholic hydroxyl group (No. 6) or of methyl substituents into the nucleus (No. 7) or into the imino-group (Nos. 8 and 9) also gave less active compounds.

Protozoacidal Drugs.

The fourth and last example of the relation which I desire to discuss to-night concerns the action of certain alkaloids in protozoal diseases. Malaria is a condition in which the blood is infested with plasmodia, and is treated by means of quinine, which has a specific action on the parasites. Amœbic dysentery is similarly due to infection with the *Entamœba histolytica*, and responds best to the action of emetine. Experiments have recently been conducted in both fields to determine whether some derivative of the alkaloids mentioned, or one of the alkaloids associated with

them in cinchona bark or ipecacuanha root respectively, have any advantages therapeutically. The line of attack has been somewhat similar in the two cases; the toxicities of the drug and a number of its derivatives to protozoa and mammals were first determined in the laboratory, and the more promising derivatives were then tested clinically.

In the case of the inquiry into the value of certain cinchona derivatives (A. C. MacGilchrist, *Ind. J. Med. Res.*, 1914—1915, **2**, 315, 336, 516; 1915—1916, **3**, 1), the relative lethality of each derivative to different species of infusoria (as representing protozoa) and to guinea-pigs (as representing mammals) was determined, with the object of finding some indication as to which derivative would be most useful for the treatment of malaria, that is, would kill the parasite and yet cause least inconvenience or harm to the host.

The results obtained are tabulated below, the substances being given in the order of their lethality to infusoria, ethylhydrocupreine hydrochloride being the most toxic. The minimum lethal dose to guinea-pigs is also given, together with formulæ designed to show the structural differences at a glance; the two pairs of stereoisomerides, quinine and quinidine, cinchonine and cinchonidine, differ in the sign of the carbon atom bearing the alcoholic hydroxyl group.

Substances in order of lethality to infusoria.	M.L.D. for guinea-pigs mg. per kilog.	Formula.
1. Ethylhydrocupreine hydrochloride	0·65	$EtO \cdot C_{17}H_{18}ON_2 \cdot CH_2 \cdot CH_3$.
2. Cinchonine sulphate	0·425	$H \cdot C_{17}H_{18}ON_2 \cdot CH:CH_2$
3. Quinine sulphate	0·525	$MeO \cdot C_{17}H_{18}ON_2 \cdot CH:CH_2$.
4. Hydroquinine hydrochloride	0·6	$MeO \cdot C_{17}H_{18}ON_2 \cdot CH_2 \cdot CH_3$.
5. Quinidine sulphate	0·4	$MeO \cdot C_{17}H_{18}ON_2 \cdot CH:CH_2$.
6. Cinchonidine sulphate	0·6	$H \cdot C_{17}H_{18}ON_2 \cdot CH:CH_2$.

From these results, it appeared that ethylhydrocupreine, in which the vinyl group of quinine is reduced, whilst ethoxyl takes the place of methoxyl, was a promising subject for clinical trial in malaria. On a clinical comparison, however, the order of their value was found to be as follows:

1. Hydroquinine hydrochloride.
2. { Cinchonine sulphate.
     Quinine sulphate.
     Quinidine sulphate.
5. Ethylhydrocupreine hydrochloride.
6. Cinchonidine sulphate.

In the case of the alkaloids of ipecacuanha, determinations of the relative toxicity of a number of compounds to free living amœbæ gave the following results (Pyman and Wenyon, *J. Pharmacol.*, 1917, in the press). Emetine, cephaeline, *N*-methyl-

emetine, and N-methylcephaeline were approximately equally amœbacidal; N-methylemetine methochloride, rubremetine hydrochloride, noremetine, and the hydrochloride B,

$$C_{20}H_{27}O_3NCl_2,HCl,5H_2O,$$

obtained by the oxidation of cephaeline, were inferior to these, whilst psychotrine sulphate was much inferior. These results indicate that the full amœbacidal action characteristic of emetine is only exhibited when the nucleus is intact. The exact constitution of the nucleus of these alkaloids is at present unknown, but it is certainly present intact and fully reduced in emetine, cephaeline, N-methylemetine, N-methylcephaeline, and noremetine, for these substances are interconvertible in a simple manner, differing only in the number of methyl groups attached to the oxygen and nitrogen atoms of the molecule.

$$C_{25}H_{27}\begin{cases}(OH)_4 \\ NH \\ N\end{cases} \qquad C_{25}H_{27}\begin{cases}OH \\ (OMe)_3 \\ NH \\ N\end{cases} \qquad C_{25}H_{27}\begin{cases}(OMe)_4 \\ NH \\ N\end{cases}$$

Noremetine. Cephaeline. Emetine.

$$C_{25}H_{25}\begin{cases}OH \\ (OMe)_3 \\ NH \\ N\end{cases} \qquad C_{25}H_{27}\begin{cases}OH \\ (OMe)_3 \\ NMe \\ N\end{cases} \qquad C_{25}H_{27}\begin{cases}(OMe)_4 \\ NMe \\ N\end{cases}$$

Psychotrine. N-Methylcephaeline. N-Methylemetine.
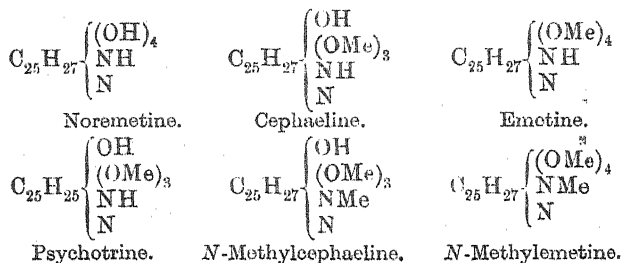
It is interesting to note that four of these compounds were very active. The inferiority of noremetine may conceivably be due to the fact that this compound contains four hydroxyl groups in place of the four methoxyl groups of emetine, for Laidlaw (*loc. cit.*) has shown that amongst other *iso*quinoline derivatives a similar change of constitution produces an alteration in physiological action. N-Methylemetine methochloride is a biquaternary salt, and, as such, a difference in its action from that of the parent tertiary base is not surprising. The fact that the hydrochloride B still retains some amœbacidal properties is interesting, because of the comparatively simple constitution of this substance, which is devoid of the guaiacol residue and one of the nitrogen atoms of cephaeline. The two remaining substances, rubremetine and psychotrine, are not fully saturated, rubremetine hydrochloride containing eight hydrogen atoms fewer than emetine hydrochloride, whilst psychotrine contains two atoms of hydrogen fewer than cephaeline.

Some of the above compounds and certain others have also been tested on *Entamœba histolytica* in vitro (Dale and Dobell, *J. Pharmacol.*, 1917, in the press), and here again emetine, cephaeline,

and *N*-methylemetine proved to be active, as was also the *O*-methyl ether of psychotrine (which had not been tested on free living amœbæ), whilst psychotrine again proved to have only a slight action.

It is curious to contrast the similarity of action between cephaeline and its methyl ether, emetine, with the difference between psychotrine and its methyl ether. The toxicity of many of the above compounds was determined, and the laboratory results indicated that *N*-methylemetine and *O*-methylpsychotrine were less toxic than emetine to mammals. Since they were at the same time equal to emetine in amœbacidal properties, it was thought that they might prove to be superior to this alkaloid in the treatment of amœbic dysentery, but unfortunately clinical trials have shown that this is not the case (G. C. Low, *Brit. Med. J.*, November 13th, 1915; C. M. Wenyon and F. W. O'Connor, *J. Roy. Army Med. Corps*, 1917, **28**, 473; M. W. Jepps and J. C. Meakins, *Brit. Med. J.*, November 17th, 1917, 648).

A review of the subjects discussed to-night leads to the conclusion that it is very difficult to improve upon naturally occurring active principles, the use of which in medicine is due to accumulated experience. In point of maximum effect, none of the natural compounds discussed to-night—hyoscyamine, cocaine, adrenaline, quinine, emetine—is surpassed by its derivatives; but, on the other hand, it has been possible in some of the cases to prepare derivatives or synthetic analogues which have proved to be of service in medicine.

In conclusion, I should like to thank Dr. H. H. Dale, F.R.S., of the staff of the Medical Research Committee, for help on the physiological side, and Dr. H. A. D. Jowett for his collaboration in the previous paper, which forms the basis of much of the work recorded above.

INDEX OF AUTHORS' NAMES.

TRANSACTIONS. 1917.

INDEX OF SUBJECTS.

TRANSACTIONS. 1917.

Single organic compounds of known empirical formula will be found in the
Formula Index, p. 1139.

FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

C_1 Group.

CH$_4$ Methane, electrical ignition of mixtures of air and (WHEELER), 411.

1 II

CHN Hydrocyanic acid, sodium salt, hydrolysis of (WORLEY and BROWNE), 1057.

CH$_2$O Formaldehyde, action of ammonium chloride with (WERNER), 844.

CH$_2$O$_2$ Formic acid, kinetics of oxidation of, and its salts (DHAR), 707.

CH$_2$N$_2$ Cyanamide, constitution of (COLSON), 554.

CH$_5$N Methylamine, preparation of (WERNER), 844.

1 III

CH$_4$ON$_2$ Carbamide, decomposition of, by nitrous acid (WERNER), 863.

CH$_4$N$_2$S Thiocarbamide, salts of (DIXON), 684; compounds of alkyl esters with (TAYLOR), 650.

C_2 Group.

C$_2$H$_2$ Acetylene, ignition of mixtures of air and (HAWARD and SASTRY), 841.

C$_2$H$_4$ Ethylene, action of bromine water on (READ and WILLIAMS), 240.

2 II

C$_2$H$_2$O$_4$ Oxalic acid, kinetics of oxidation of, and its salts (DHAR), 707.

C$_2$H$_7$N Dimethylamine, preparation of (WERNER), 844.

2 III

C$_2$H$_7$ON Acetaldehyde-ammonia, action of, on quinones (GHOSH), 608.

2 IV

C$_2$H$_7$O$_3$N$_3$S Substance, from thiocarbamide and methyl nitrate (TAYLOR), 657.

C_3 Group.

C$_3$H$_6$O Acetone, propagation of flame in mixtures of air and (WHEELER and WHITAKER), 267; compounds of calcium chloride and (BAGSTER), 494.

C$_3$H$_6$O$_2$ Methyl acetate, effect of sucrose on the hydrolysis of (GRIFFITH, LAMBLE, and LEWIS), T., 390.

3 III

C$_3$H$_7$N$_3$S$_2$ Substance, from thiocarbamide and methyl thiocyanate (TAYLOR), 659.

C_4 Group.

$C_4H_{10}O$ Ethyl ether, compound of ferric chloride with (FORSTER, COOPER, and YARROW), 809.

4 III

$C_4H_4O_2S$ $\alpha\beta$-Thiocrotonic acid, and its salts (RÂY and DEY), 510.

4 IV

$C_4H_5O_2IS$ β-Iodo-$\alpha\beta$-thiobutyric acid, silver salt (RÂY and DEY), 512.

$C_4H_{14}O_4N_4S_2$ Substance, from methyl sulphate and thiocarbamide (TAYLOR), 655.

C_5 Group.

$C_5H_8O_2$ Acetylacetone, action of aromatic amines on (TURNER), 1.

C_6 Group.

C_6H_6 Benzene, reaction of phthalyl chloride with (COPISAROW), 10.

6 II

$C_6H_6O_2$ Catechol, orientation and scission of substituted ethers of (JONES and ROBINSON), 903; (G. M. and R. ROBINSON), 929.

$C_6H_8N_2$ Phenylhydrazine, action of, on opianic, nitro-opianic, and phthalonic acids (MITTER and SEN), 988.

6 III

$C_6H_4ON_2$ Benzisooxadiazole, preparation of (GREEN and ROWE), 618.

6 IV

$C_6H_4O_4N_2S$ Benzenediazo-1-oxidesulphonic acids, and their salts (MORGAN and TOMLINS), 501.

Phenol-3- and -4-diazoniumsulphonates (MORGAN and TOMLINS), 503.

$C_6H_4NBr_2I$ Dibromoiodoanilines (SUDBOROUGH and LAKHUMALANI), 47.

$C_6H_{18}O_4N_4S_3$ Substance, from ethyl sulphate and thiocarbamide (TAYLOR), 656.

C_7 Group.

$C_7H_6O_6$ 2:3:4:6-Tetrahydroxybenzoic acid ($+ H_2O$) (NIERENSTEIN), 5.

7 III

$C_7H_3O_5N_3$ Substance, from diazotisation of 5-nitro-3-aminosalicylic acid (MELDOLA, FOSTER, and BRIGHTMAN), 541.

$C_7H_4O_2Cl_2$ 4:5-Dichlorocatechol methylene ether (ORR, ROBINSON, and WILLIAMS), 949.

$C_7H_4O_2Br_2$ 4:5-Dibromocatechol methylene ether (JONES and ROBINSON), 913.

$C_7H_5ON_3$ Formyl-p-phenylenediazoimide ($+ 1\frac{1}{2}H_2O$) (MORGAN and UPTON), 190.

$C_7H_6ON_2$ 5-Methylbenzisooxadiazole (GREEN and ROWE), 619.

$C_7H_8O_2Br_2$ 4:5-Dibromoguaiacol (HINDMARSH, KNIGHT, and ROBINSON), 942.

$C_7H_7O_2Br$ 5-Bromoguaiacol (HINDMARSH, KNIGHT, and ROBINSON), 941.

7 IV

$C_7H_3O_3N_2Cl$ Substance, from diazotisation of chloroaminosalicylic acid (MELDOLA, FOSTER, and BRIGHTMAN), 543.

$C_7H_3O_6N_2Cl$ 4-Chloro-5:6-dinitrocatechol methylene ether (ORR, ROBINSON, and WILLIAMS), 951.

$C_7H_4O_2ClBr$ 4-Chloro-5-bromocatechol methylene ether (ORR, ROBINSON, and WILLIAMS), 950.

$C_7H_4O_4NCl$ 4-Chloro-5-nitrocatechol methylene ether (ORR, ROBINSON and WILLIAMS), 951.

C₈ Group.

8 III

8 IV

$C_8H_7O_6N_2Br$ Bromodinitroveratroles (JONES and ROBINSON), 924; (HIND-MARSH, KNIGHT, and ROBINSON), 943.

$C_8H_8O_4NBr$ 6-Bromo-5-nitroveratrole (JONES and ROBINSON), 917.

$C_8H_9O_7NS$ Nitroveratrolesulphonic acid, potassium salt of (BROWN and ROBINSON), 953.

$C_8H_{11}O_5NS$ 3- and 5-Aminoveratrole-4-sulphonic acids (BROWN and ROBINSON), 954.

$C_8H_{18}O_4N_4S_2$ Substance, from ethyl oxalate and thiocarbamide (TAYLOR), 661.

8 V

$C_8H_6ONBr_2I$ Dibromoiodoacetanilides (SUDBOROUGH and LAKHUMALANI), 47.

$C_8H_8O_6NClS$ 5-Nitroveratrole-4-sulphonyl chloride (BROWN and ROBINSON), 953.

C_9 Group.

$C_9H_6O_5$ Phthalonic acid, action of phenylhydrazine on (MITTER and SEN), 988.

$C_9H_{16}O_7$ Substance, from trimethyl glucose and hydrocyanic acid (DENHAM and WOODHOUSE), 248.

$C_9H_{18}O_6$ Trimethyl glucose (DENHAM and WOODHOUSE), 244.

9 III

$C_9H_8O_2N_2$ 5:6-Methylenedioxy-2-methylbenziminazole (JONES and ROBINSON), 916.

$C_9H_8O_4N_2$ 5-Nitro-2:3-dimethoxybenzonitrile (GIBSON, SIMONSEN, and RAU), 76.

$C_9H_8O_5N_2$ 5-Nitro-4-acetylaminocatechol methylene ether (JONES and ROBINSON), 914.

$C_9H_8O_6N_2$ 5-Nitro-3-acetylaminosalicylic acid (MELDOLA, FOSTER, and BRIGHTMAN), 541.

$C_9H_9O_2Br$ β-Phenyl-α-bromopropionic acid, kinetics and dissociation constant of (SENTER and MARTIN), 447.

$C_9H_9O_3Br$ 5-Bromo-2-methoxyphenyl acetate (HINDMARSH, KNIGHT, and ROBINSON), 941.

$C_9H_9O_5N$ Methyl nitromethoxybenzoates (SIMONSEN and RAU), 229.

$C_9H_{10}O_6N_2$ 6-Nitro-2-amino-3:4-dimethoxybenzoic acid (GIBSON, SIMONSEN, and RAU), 75.

$C_9H_{11}O_3Br$ 6-Bromohomoveratrole (JONES and ROBINSON), 919.

$C_9H_{11}N_3S_2$ Substance, from thiocarbamide and benzyl thiocyanate (TAYLOR), 660.

$C_9H_{12}O_5N_2$ 5(or 6)-Nitro-6(or 5)-amino-1:2:4-trimethoxybenzene (JONES and ROBINSON), 926.

$C_9H_{12}O_5N_4$ 3:5-Dinitro-2:4-dimethylaminoanisole (HINDMARSH, KNIGHT, and ROBINSON), 944.

9 IV

$C_9H_8O_4NCl$ 3-Chloro-5-acetylaminosalicylic acid (MELDOLA, FOSTER, and BRIGHTMAN), 543.

$C_9H_8O_5NBr$ Bromonitroveratraldehydes (JONES and ROBINSON), 920, 923.

$C_9H_8O_5NS$ Veratric-6-sulphinide (BROWN and ROBINSON), 956.

$C_9H_{10}O_4NBr$ 6-Bromo-5-nitrohomoveratrole (JONES and ROBINSON), 919.

$C_9H_{13}O_4NS$ Homoveratrole-6-sulphonamide (BROWN and ROBINSON), 954.

C_{10} Group.

$C_{10}H_{10}O_2$ Benzoylacetone, action of aromatic amines on (TURNER), 1.

$C_{10}H_{10}O_5$ Opianic acid, action of phenylhydrazine on (MITTER and SEN), 988.

C$_{12}$ Group.

C$_{12}$H$_{16}$O$_3$ Methylzingerone (NOMURA), 772; (LAPWORTH, PEARSON, and ROYLE), 786.

C$_{12}$H$_{16}$O$_5$ Tetramethoxyacetophenone (NIERENSTEIN), 7.

C$_{12}$H$_{16}$O$_6$ Methyl 2:3:4:6-tetramethoxybenzoate (NIERENSTEIN), 6.

C$_{12}$H$_{18}$O$_9$ Caramelan, preparation and constitution of (CUNNINGHAM and DORÉE), 593.

C$_{12}$H$_{22}$O$_{11}$ Sucrose, effect of methyl acetate on the inversion of (GRIFFITH, LAMBLE, and LEWIS), 390.

12 III

C$_{12}$H$_6$O$_{11}$N$_6$ 2:4:6:3′:5′-Pentanitro-4′-hydroxydiphenylamine (MELDOLA, FOSTER, and BRIGHTMAN), 550.

C$_{12}$H$_8$O$_7$N$_4$ 2:4:?-Trinitro-4′-hydroxydiphenylamine (MELDOLA, FOSTER, and BRIGHTMAN), 548.

Substance, from 2:4:6-trinitro-4′-hydroxydiphenylamine and nitric acid (MELDOLA, FOSTER, and BRIGHTMAN), 550.

C$_{12}$H$_9$O$_5$N$_3$ 2:4-Dinitro-4′-hydroxydiphenylamine (MELDOLA, FOSTER, and BRIGHTMAN), 547.

C$_{12}$H$_{11}$O$_4$N Ethyl α-cyanocaffeate (LAPWORTH and WYKES), 798.

C$_{12}$H$_{13}$O$_8$N$_3$ 4:5-Dinitro-3-diacetylaminoveratrole (GIBSON, SIMONSEN, and RAU), 79.

C$_{12}$H$_{14}$O$_{17}$N$_4$ Caramelan tetranitrate (CUNNINGHAM and DORÉE), 595.

C$_{12}$H$_{17}$O$_3$N Methylzingeroneoxime (NOMURA), 773; (LAPWORTH, PEARSON, and ROYLE), 786.

C$_{13}$ Group.

C$_{13}$H$_{12}$O$_4$ 3:6:3′:6′-Tetrahydroxydiphenylmethane, preparation of (GHOSH and WATSON), 825.

C$_{13}$H$_{16}$O$_4$ Acetylzingerone (NOMURA), 772.

C$_{13}$H$_{18}$O$_3$ Ethylzingerone (NOMURA), 773.

13 III

C$_{13}$H$_9$ON$_3$ Benzoyl-p-phenylenediazoimide (MORGAN and UPTON), 195.

C$_{13}$H$_{10}$O$_7$N$_4$ p-Nitrobenzyl*iso*picramic acid (MELDOLA, FOSTER, and BRIGHTMAN), 553.

C$_{13}$H$_{11}$O$_5$N$_3$ 2:4-Dinitro-4′-hydroxydiphenylmethylamine (MELDOLA, FOSTER, and BRIGHTMAN), 549.

C$_{13}$H$_{13}$O$_4$N Ethyl vanillylidenecyanoacetate (LAPWORTH and WYKES), 796.

C$_{13}$H$_{21}$O$_2$N β-Diethylamino-β′-phenoxy*iso*propyl alcohol and its hydrochloride (PYMAN), 170.

C$_{14}$ Group.

C$_{14}$H$_{14}$S Benzyl sulphide, compound of ferric chloride with (FORSTER, COOPER, and YARROW), 809.

C$_{14}$H$_{18}$O$_5$ Ethylcarbonatozingerone (LAPWORTH, PEARSON, and ROYLE), 785; (LAPWORTH and WYKES), 794.

14 III

C$_{14}$H$_9$O$_{10}$N$_5$ 2:4:?:?-Tetranitro-4′-hydroxyacetyldiphenylamine (MELDOLA, FOSTER, and BRIGHTMAN), 549.

C$_{14}$H$_{10}$O$_8$N$_4$ 2:4:?-Trinitro-4′-hydroxyacetyldiphenylamine (MELDOLA, FOSTER, and BRIGHTMAN), 548.

C$_{14}$H$_{10}$O$_4$N$_2$ 4:5:4′:5′-Dimethylenetetraoxyazobenzene (ROBINSON), 113.

C$_{14}$H$_{11}$O$_6$N$_3$ Acetyl derivative of 2:4-dinitro-4′-hydroxydiphenylamine (MELDOLA, FOSTER, and BRIGHTMAN), 548.

C_{15} Group.

C_{16} Group.

$C_{16}H_{14}O_4N_2$ Phenylazomeconin (MITTER and SEN), 991.

$C_{16}H_{16}O_4N_2$ Substance, from phenylhydrazine and opianic acid (MITTER and SEN), 991.

$C_{16}H_{16}O_9N_4$ 6:6'-Dinitroazoxyveratrole (ROBINSON), 116.

$C_{16}H_{17}O_7N_3$ 6-Nitroazoxyveratrole (ROBINSON), 115.

$C_{16}H_{18}O_5N_2$ Azoxyveratrole (ROBINSON), 114.

16 IV

$C_{16}H_{14}ONBr$ Benzoylacetone-p-bromoanilide (TURNER), 3.

$C_{16}H_{16}O_6N_4S$ 6-Nitroveratryl-4:5-thiotriazoveratrole   (JONES   and   ROBINSON), 925.

$C_{16}H_{17}O_5N_2Br$ 6-Bromoazoxyveratrole (ROBINSON), 115.

$C_{16}H_{18}O_4N_4S$ 6-Aminoveratryl-4:5-thiotriazoveratrole   (JONES   and   ROBINSON), 925.

$C_{16}H_{22}O_4N_4S_3$ Substance, from benzyl sulphate and thiocarbamide (TAYLOR), 656.

C_{17} Group.

$C_{17}H_{11}ON_3$ Benzoyl-1:4-naphthylenediazoimide (MORGAN and UPTON), 196.

$C_{17}H_{12}O_4N_2$ 4-Hydroxy-3-carboxybenzeneazo-β-naphthol (MELDOLA, FOSTER, and BRIGHTMAN), 538.

$C_{17}H_{12}O_7N_4$ 4:5-Dinitro-2-hydroxy-1-methoxy-3-azo-β-naphthol   (GIBSON, SIMONSEN, and RAU), 82.

$C_{17}H_{13}O_2N_3$ Formyl-β-aminobenzeneazo-β-naphthol (MORGAN and UPTON), 193.

$C_{17}H_{16}O_4N_2$ 8-p-Nitrobenzoyl-1-methyl-1:2:3:4-tetrahydroquinoline (PYMAN), 171.

$C_{17}H_{17}O_2N$ 8-Benzoyloxy-1-methyl-1:2:3:4-tetrahydroquinoline (PYMAN), 171.

$C_{17}H_{21}ON$ d- and l-Phenylbenzylmethylallylammonium   hydroxide, salts of, with bromocamphorsulphonic acids (REILLY), 20.

$C_{17}H_{21}O_4N$ Cocaine, compound of mercuric nitrite and (RÂY), 509.

17 IV

$C_{17}H_{11}O_4N_2Cl$ 5-Chloro-4-hydroxy-3-carboxybenzeneazo-β-naphthol (MELDOLA, FOSTER, and BRIGHTMAN), 543.

C_{18} Group.

$C_{18}H_{12}O_2$ Substance, from anthraquinone and acetaldehyde-ammonia (GHOSH), 611.

$C_{18}H_{18}O_4$ Benzoylzingerone (NOMURA), 771.

18 III

$C_{18}H_{18}O_7N_2$ Azoxyveratraldehyde (ROBINSON), 121.

$C_{18}H_{21}O_3N$ Codeine, compound of mercuric nitrite and (RÂY), 508.

18 IV

$C_{18}H_{22}O_4N_4S_2$ Substance, from benzyl oxalate and thiocarbamide (TAYLOR), 661.

C_{19} Group.

$C_{19}H_{14}O_5$ Trihydroxyaurin (GHOSH and WATSON), 826.

$C_{19}H_{14}O_7$ Trihydroxy-9-o-p-dihydroxyphenyl-6-fluorones   (GHOSH   and   WATSON), 828.

19 III

$C_{19}H_{12}O_5Cl_2$ Di-6-chloromethylenedioxystyryl ketone (ORR, ROBINSON, and WILLIAMS), 948.

$C_{19}H_{22}ON_2$ Cinchonidine, compound of mercuric nitrite and (RÂY), 508.

C$_{20}$ Group.

$C_{23}H_{22}O_2N_2$ 3-Dimethylamino-9-p-hydroxyphenyl-6-dimethylfluorime (GHOSH and WATSON), 827.

$C_{23}H_{22}O_3N_2$ 3-Dimethylamino-9-o-p-dihydroxyphenyl-6-dimethylfluorime (GHOSH and WATSON), 827.

$C_{23}H_{24}ON_2$ 4-Hydroxymalachite-green (GHOSH and WATSON), 826.

$C_{23}H_{24}O_2N_2$ 2:4-Dihydroxymalachite-green (GHOSH and WATSON), 826.
3:6-Tetramethyldiamino-9-p-hydroxyphenylxanthene   (GHOSH   and WATSON), 827.

$C_{23}H_{26}O_4N_2$ Brucine, compound of mercuric nitrite and (RAY), 509.

C_{24} Group.

$C_{24}H_{26}O_{13}$ Caramelin (CUNNINGHAM and DORÉE), 602.

24 III

$C_{24}H_{20}O_2N_2$ 2:3-Diethoxyphenanthraphenazine (G. M. and R. ROBINSON), 934.

$C_{24}H_{21}O_5N$ Dipiperonylidenetropinone (ROBINSON), 765.

C_{26} Group.

$C_{26}H_{20}O_2$ Tetraphenylmethane-o-carboxylic acid, and its salts (COPISAROW), 17.

$C_{26}H_{32}O_4$ Menthyl hydrogen diphenylsuccinates (WREN and STILL), 521.

C_{28} Group.

$C_{28}H_{18}O_5N_2$ 3:4-Di-p-nitrotetraphenylfuran (FRANCIS), 1039.

$C_{28}H_{22}O_5N_6$ Azoxypiperonal diphenylhydrazone (ROBINSON), 118.

$C_{28}H_{25}O_5N$ Anhydroberberineacetophenone (G. M. and R. ROBINSON), 968.

C_{29} Group.

$C_{29}H_{36}O_4N_2$ Emetamine, and its salts (PYMAN), 442.

$C_{29}H_{38}O_4N_2$ Methylpsychotrine, and its salts (PYMAN), 431.

C_{30} Group.

$C_{30}H_{50}$ Spinacene (CHAPMAN), 56.

30 II

$C_{30}H_{24}N_4$ Hydrazone of substance, $C_{18}H_{12}O_2$ (GHOSH), 612.

$C_{30}H_{50}Br_{12}$ Spinacene dodecabromide (CHAPMAN), 63.

30 III

$C_{30}H_{26}O_4N_2$ Benzoyl derivative of 3-dimethylamino-9-o-p-dihydroxyphenyl-6-dimethylfluorime (GHOSH and WATSON), 28.

$C_{30}H_{28}O_2N_2$ Benzoyl derivative of 3:6-tetramethyldiamino-9-p-hydroxyphenylxanthene (GHOSH and WATSON), 827.

$C_{30}H_{28}O_{10}N_2$ Substance, from caramelan and phenylhydrazine (CUNNINGHAM and DORÉE), 597.

$C_{30}H_{38}O_{15}N_2$ Substance, from caramelan and phenylhydrazine (CUNNINGHAM and DORÉE), 597.

$C_{30}H_{42}O_4N_2$ Methylemetine, and its salts (PYMAN), 444.

$C_{30}H_{50}O_{12}N_6$ Spinacene nitrosate (CHAPMAN), 67.

30 IV

$C_{30}H_{50}O_3N_3Cl_3$ Spinacene trinitrosochloride (CHAPMAN), 64.

$C_{30}H_{50}O_6N_6Cl_6$ Spinacene hexanitrosochloride (CHAPMAN), 66.

C₃₂ Group.

C₃₂H₂₈O₂N₂ Dibenzoyl*iso*propylidenebenzidine (TURNER), 4.
C₃₂H₄₆O₄N₂ Methylemetinemethine, and its salts (PYMAN), 445.

C₃₅ Group.

C₃₅H₂₂O₁₀ 2:3:4:6-Tetrabenzoyloxybenzoic acid (NIERENSTEIN), 6.

35 IV

C₃₅H₆₀O₃N₄Cl₂ Spinacene dinitrosochloride nitrolpiperidide (CHAP-
    MAN), 65.

C₃₆ Group.

C₃₆H₅₀O₄ Dimethyl diphenylsuccinates (WREN and STILL), 520.

36 III

C₃₆H₄₂O₅N₂ Benzoylmethylpsychotrine (PYMAN), 436.
C₃₆H₄₄O₅N₂ Benzoyl*iso*emetine (PYMAN), 439.

C₃₇ Group.

C₃₇H₄₃O₂₀N₃ Substance, from caramelan and semicarbazide (CUNNINGHAM and
    DORÉE), 598.

37 IV

C₃₇H₅₈O₃N₄Cl₂ Spinacene dinitrosochloride nitrobenzylamide (CHAP-
    MAN), 66.

C₄₀ Group.

C₄₀H₃₄O₁₃ Caramelan tetrabenzoate (CUNNINGHAM and DORÉE), 595.

C₄₅ Group.

C₄₅H₈₀O₃N₆ Spinacene trinitrolpiperidide (CHAPMAN), 65.

C₅₁ Group.

C₅₁H₇₄O₃N₆ Spinacene trinitrolbenzylamide (CHAPMAN), 66.

ERRATA.

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Page	Line	
17	24	*for* "diphenyphthalide" *read* "diphenylphthalide."
42	2	,, "hydroyl" *read* "hydroxyl."
68	12*	,, "$C_{28}H_{58}$" *read* "$C_{30}H_{62}$."

104   15   ,,

107   11*   ,,   "Hg = 6·14" *read* "Hg = 69·14."

168   1   ,,   "devoid of local anæsthetic properties (compare S. Fränkel, 'Die Arzneimittel-Synthese,' 1912, p. 349), but" *read* "having local anæsthetic properties in a lesser degree (Ehrlich and Einhorn, *Ber.*, 1894, **27**, 1870), and."

243   15*   ,,   "water" *read* "oxygen."

260   13*   ,,

267   15   ,,   "$\left(Co\dfrac{5NH_3}{Cl}\right)Cl$" *read* "$\left(Co\dfrac{5NH_3}{Cl}\right)Cl_2$"

511   7*   ,,

566   7*   read the percentages of primary amine at the foot of Fig. 2 in reverse order, *i.e.* "7, 6, 5, 4, 3, 2, 1, 0."

650   1   *for* "s-*Alkylthiocarbamides*" read "S-*Alkylthiocarbamides.*"

655   8*   ,,   "$C_{11}H_{14}O_4N_{11}S_2$" *read* "$C_4H_{14}O_4N_4S_2$."

791   10   ,,

828   13   ,,   "$C_{30}H_{27}O_4N_2$" *read* "$C_{30}H_{26}O_4N_2$."

905   7*   ,,

908   1*   ,,

946   16   ,,   "displaement" *read* "displacement."
1070   4*   ,,   "*pentasulphate*" read "*pentasulphide.*"
1087   16   ,,   "156·3 μ" *read* "156·3 $\mu\mu$."

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* From bottom.

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